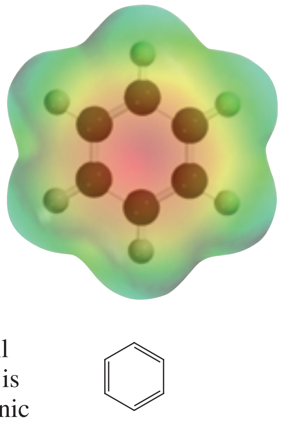
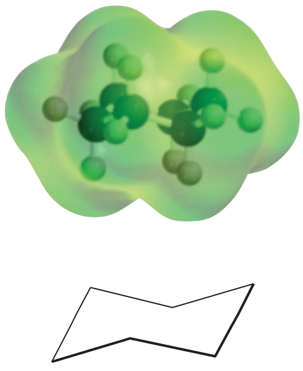
7

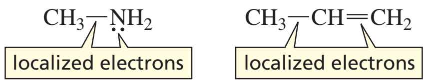
Electron Delocalization and Resonance • More About Molecular Orbital Theory



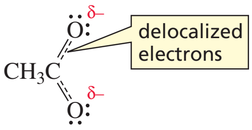


As you continue your study of organic chemistry, you will notice that the concept of having delocalized electrons is invoked frequently to explain the behavior of organic compounds. For example, in Chapter 8 you will see that having delocalized electrons causes certain dienes to form products that would not be expected on the basis of what you have learned about electrophilic addition reactions in Chapters 3–6. Electron delocalization is such an important concept that this entire chapter is devoted to it.

Electrons that are restricted to a particular region are called **localized electrons**. Localized electrons either belong to a single atom or are confined to a bond between two atoms.



Not all electrons are confined to a single atom or bond. Many organic compounds contain *delocalized* electrons. **Delocalized electrons** neither belong to a single atom nor are confined to a bond between two atoms, but are shared by three or more atoms. You were first introduced to delocalized electrons in Section 1.19, where you saw that the two electrons represented by the π bond of the COO^- group are shared by three atoms—the carbon and both oxygen atoms. The dashed lines indicate that the two electrons are delocalized over three atoms.



In this chapter, you will learn to recognize compounds that contain delocalized electrons and to draw structures that represent the electron distribution in molecules with delocalized electrons. You will also be introduced to some of the special characteristics of compounds that have delocalized electrons. You will then be able to understand the wide-ranging effects that delocalized electrons have on the reactivity of organic compounds. We begin by taking a look at benzene, a compound whose properties chemists could not explain until they recognized that electrons in organic molecules could be delocalized.

7.1 Delocalized Electrons: The Structure of Benzene

The structure of benzene puzzled early organic chemists. They knew that benzene had a molecular formula of C_6H_6, that it was an unusually stable compound, and that it did not undergo the addition reactions characteristic of alkenes (Section 3.6). They also knew the following facts:

1. When a different atom is substituted for one of the hydrogen atoms of benzene, only one product is obtained.
2. When the substituted product undergoes a second substitution, three products are obtained.

$$C_6H_6 \xrightarrow[\text{with an X}]{\text{replace a hydrogen}} C_6H_5X \xrightarrow[\text{with an X}]{\text{replace a hydrogen}} C_6H_4X_2 + C_6H_4X_2 + C_6H_4X_2$$

one monosubstituted compound

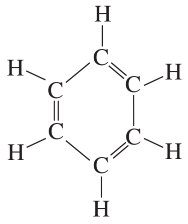
three disubstituted compounds

What kind of structure might we predict for benzene if we knew only what the early chemists knew? The molecular formula (C_6H_6) tells us that benzene has eight fewer hydrogens than an acyclic (noncyclic) alkane with six carbons ($C_nH_{2n+2} = C_6H_{14}$). Benzene, therefore, has a degree of unsaturation of four (Section 3.1). This means that benzene is either an acyclic compound with four π bonds, a cyclic compound with three π bonds, a bicyclic compound with two π bonds, a tricyclic compound with one π bond, or a tetracyclic compound.

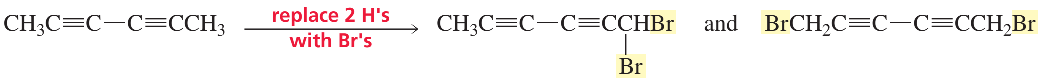
For every *two* hydrogens that are missing from the general molecular formula C_nH_{2n+2}, a hydrocarbon has either a π bond or a ring.

Because only one product is obtained regardless of which of the six hydrogens is replaced with another atom, we know that all the hydrogens must be identical. Two structures that fit these requirements are shown here:

$CH_3C{\equiv}C{-}C{\equiv}CCH_3$

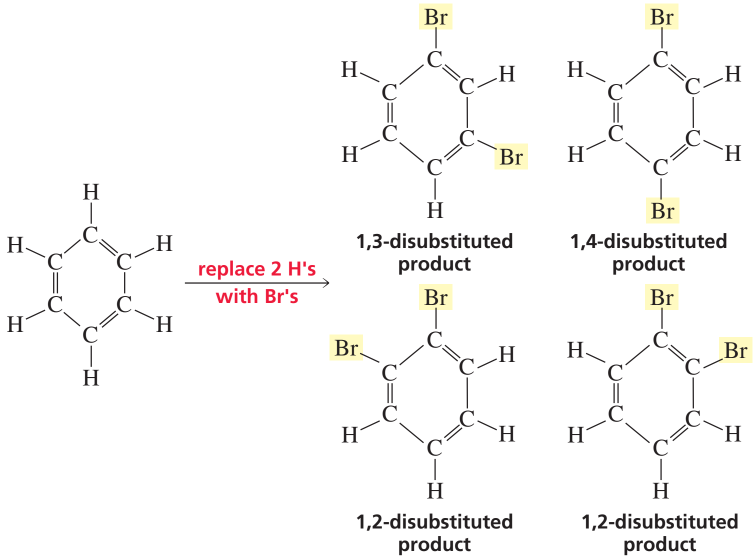


Neither of these structures is consistent with the observation that three compounds are obtained if a second hydrogen is replaced with another atom. The acyclic structure yields two disubstituted products.



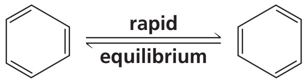
$$CH_3C{\equiv}C{-}C{\equiv}CCH_3 \xrightarrow[\text{with Br's}]{\text{replace 2 H's}} CH_3C{\equiv}C{-}C{\equiv}C\underset{\displaystyle Br}{\underset{|}{C}}HBr \quad \text{and} \quad BrCH_2C{\equiv}C{-}C{\equiv}CCH_2Br$$

The cyclic structure, with alternating single and slightly shorter double bonds, yields four disubstituted products—a 1,3-disubstituted product, a 1,4-disubstituted product, and two 1,2-disubstituted products—because the two substituents can be placed either on two adjacent carbons joined by a single bond or on two adjacent carbons joined by a double bond.



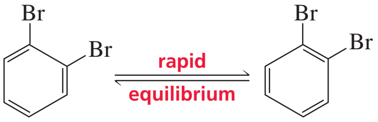
3-D Molecules:
1,2-Difluorobenzene;
1,3-Difluorobenzene;
1,4-Difluorobenzene

In 1865, the German chemist Friedrich Kekulé suggested a way of resolving this dilemma. He proposed that benzene was not a single compound, but a mixture of two compounds in rapid equilibrium.

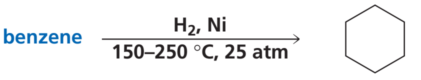


Kekulé structures of benzene

Kekule's proposal explained why only three disubstituted products are obtained when a monosubstituted benzene undergoes a second substitution. According to Kekulé, there actually *are* four disubstituted products, but the two 1,2-disubstituted products interconvert too rapidly to be distinguished and separated from each other.



The Kekulé structures of benzene account for the molecular formula of benzene and for the number of isomers obtained as a result of substitution. However, they fail to account for the unusual stability of benzene and for the observation that the double bonds of benzene do not undergo the addition reactions characteristic of alkenes. That benzene had a six-membered ring was confirmed in 1901, when Paul Sabatier (Section 4.11) found that the hydrogenation of benzene produced cyclohexane. This, however, still did not solve the puzzle of benzene's structure.

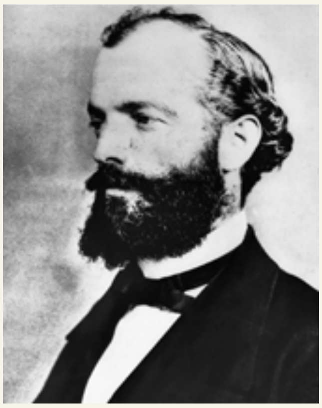


cyclohexane

Controversy over the structure of benzene continued until the 1930s, when the new techniques of X-ray and electron diffraction produced a surprising result: They showed that *benzene is a planar molecule and the six carbon–carbon bonds have the same length*. The length of each carbon–carbon bond is 1.39 Å, which is shorter than a carbon–carbon single bond (1.54 Å) but longer than a carbon–carbon double bond

KEKULÉ'S DREAM

Friedrich August Kekulé von Stradonitz (1829–1896) was born in Germany. He entered the University of Giessen to study architecture, but switched to chemistry after taking a course in the subject. He was a professor of chemistry at the University of Heidelberg, at the University of Ghent in Belgium, and then at the University of Bonn. In 1890, he gave an extemporaneous speech at the twenty-fifth-anniversary celebration of his first paper on the cyclic structure of benzene. In this speech, he claimed that he had arrived at the Kekulé structures as a result of dozing off in front of a fire while working on a textbook. He dreamed of chains of carbon atoms twisting and turning in a snakelike motion, when suddenly the head of one snake seized hold of its own tail and formed a spinning ring. Recently, the veracity of his snake story has been questioned by those who point out that there is no written record of the dream from the time he experienced it in 1861 until the time he related it in 1890. Others counter that dreams are not the kind of evidence one publishes in scientific papers, although it is not uncommon for scientists to report moments of creativity through the subconscious, when they were not thinking about science. Also, Kekulé warned against publishing dreams when he said, "Let us learn to dream, and perhaps then we shall learn the truth. But let us also beware not to publish our dreams until they have been examined by the wakened mind." In 1895, he was made a nobleman by Emperor William II. This allowed him to add "von Stradonitz" to his name. Kekulé's students received three of the first five Nobel Prizes in chemistry: van't Hoff in 1901 (page 194), Fischer in 1902 (page 187), and Baeyer in 1905 (page 94).



Friedrich August Kekulé von Stradonitz

(1.33 Å; Section 1.14). In other words, benzene does not have alternating single and double bonds.

If the carbon–carbon bonds all have the same length, they must also have the same number of electrons between the carbon atoms. This can be so, however, only if the π electrons of benzene are delocalized around the ring, rather than each pair of π electrons being localized between two carbon atoms. To better understand the concept of delocalized electrons, we'll now take a close look at the bonding in benzene.

PROBLEM 1◆

a. How many monosubstituted products would each of the following compounds have? (Notice that each compound has the same molecular formula as benzene.)

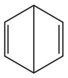
1. $HC{\equiv}CC{\equiv}CCH_2CH_3$
2. $CH_2{=}CHC{\equiv}CCH{=}CH_2$

b. How many disubstituted products would each of the preceding compounds have? (Do not include stereoisomers.)

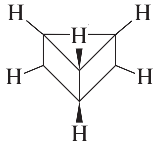
c. How many disubstituted products would each of the compounds have if stereoisomers are included?

PROBLEM 2

Between 1865 and 1890, other possible structures were proposed for benzene, two of which are shown here:



Dewar benzene



Ladenburg benzene

Considering what nineteenth-century chemists knew about benzene, which is a better proposal for the structure of benzene, Dewar benzene or Ladenburg benzene? Why?

Sir James Dewar (1842–1923) *was born in Scotland, the son of an innkeeper. After studying under Kekulé, he became a professor at Cambridge University and then at the Royal Institution in London. Dewar's most important work was in the field of low-temperature chemistry. He used double-walled flasks with evacuated space between the walls in order to reduce heat transmission. These flasks are now called Dewar flasks—better known to nonchemists as thermos bottles.*

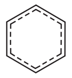
Albert Ladenburg (1842–1911) *was born in Germany. He was a professor of chemistry at the University of Kiel.*

7.2 The Bonding in Benzene

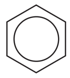
Benzene is a planar molecule. Each of its six carbon atoms is sp^2 hybridized. An sp^2 hybridized carbon has bond angles of 120°—identical to the size of the angles of a planar hexagon. Each of the carbons in benzene uses two sp^2 orbitals to bond to two other carbons; the third sp^2 orbital overlaps the *s* orbital of a hydrogen (Figure 7.1a). Each carbon also has a *p* orbital at right angles to the sp^2 orbitals. Because benzene is planar, the six *p* orbitals are parallel (Figure 7.1b). The *p* orbitals are close enough for side-to-side overlap, so each *p* orbital overlaps the *p* orbitals on both adjacent carbons. As a result, the overlapping *p* orbitals form a continuous doughnut-shaped cloud of electrons above, and another doughnut-shaped cloud of electrons below, the plane of the benzene ring (Figure 7.1c). The electrostatic potential map (Figure 7.1d) shows that all the carbon–carbon bonds have the same electron density.

Each of the six π electrons, therefore, is localized neither on a single carbon nor in a bond between two carbons (as in an alkene). Instead, each π electron is shared by all six carbons. The six π electrons are delocalized—they roam freely within the doughnut-shaped clouds that lie over and under the ring of carbon atoms. Consequently, benzene can be represented by a hexagon containing either dashed lines or a circle, to symbolize the six delocalized π electrons.

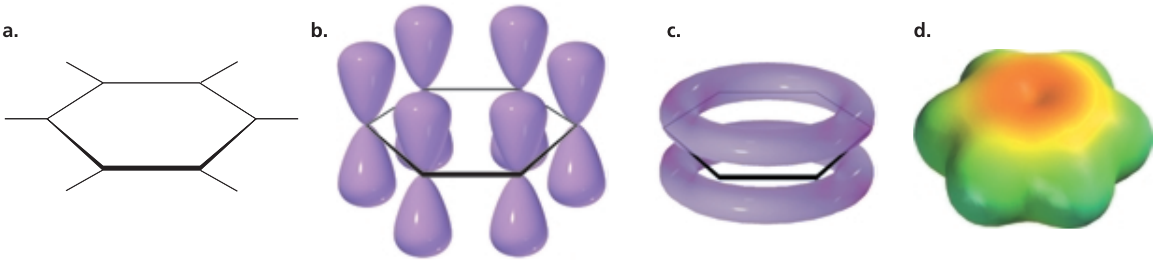
3-D Molecule: Benzene



or



This type of representation makes it clear that there are no double bonds in benzene. We see now that Kekulé's structure for benzene was pretty close to the correct structure. The actual structure of benzene is a Kekulé structure with delocalized electrons.

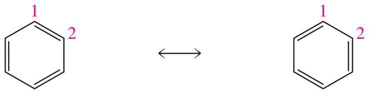


▲ **Figure 7.1**
(a) The carbon–carbon and carbon–hydrogen σ bonds in benzene.
(b) The *p* orbital on each carbon of benzene can overlap with two adjacent *p* orbitals.
(c) The clouds of electrons above and below the plane of the benzene ring.
(d) The electrostatic potential map for benzene.

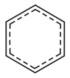
7.3 Resonance Contributors and the Resonance Hybrid

A disadvantage to using dashed lines to represent delocalized electrons is that they do not tell us how many π electrons are present in the molecule. For example, the dashed lines inside the hexagon in the representation of benzene indicate that the π electrons are shared equally by all six carbons and that all the carbon–carbon bonds have the same length, but they do not show how many π electrons are in the ring. Consequently, chemists prefer to use structures with localized electrons to approximate the actual structure that has delocalized electrons. The approximate structure with localized electrons is called a **resonance contributor**, a **resonance structure**, or a **contributing**

resonance structure. The actual structure with delocalized electrons is called a **resonance hybrid**. Notice that it is easy to see that there are six π electrons in the ring of each resonance contributor.



resonance contributor **resonance contributor**

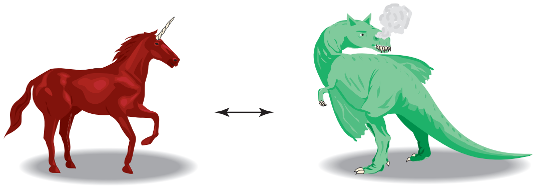


resonance hybrid

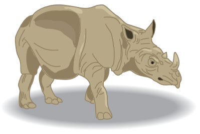
Resonance contributors are shown with a double-headed arrow between them. The double-headed arrow does *not* mean that the structures are in equilibrium with one another. Rather, it indicates that the actual structure lies somewhere between the structures of the resonance contributors. Resonance contributors are merely a convenient way to show the π electrons; they do not depict any real electron distribution. For example, the bond between C-1 and C-2 in benzene is not a double bond, although the resonance contributor on the left implies that it is. Nor is it a single bond, as represented by the resonance contributor on the right. Neither of the contributing resonance structures accurately represents the structure of benzene. The actual structure of benzene—the resonance hybrid—is given by the average of the two resonance contributors.

Electron delocalization is shown by double-headed arrows ($\leftrightarrow$). Equilibrium is shown by two arrows pointing in opposite directions ($\rightleftharpoons$).

The following analogy illustrates the difference between resonance contributors and the resonance hybrid. Imagine that you are trying to describe to a friend what a rhinoceros looks like. You might tell your friend that a rhinoceros looks like a cross between a unicorn and a dragon. The unicorn and the dragon don't really exist, so they are like the resonance contributors. They are not in equilibrium: A rhinoceros does not jump back and forth between the two resonance contributors, looking like a unicorn one minute and a dragon the next. The rhinoceros is real, so it is like the resonance hybrid. The unicorn and the dragon are simply ways to represent what the actual structure—the rhinoceros—looks like. *Resonance contributors, like unicorns and dragons, are imaginary, not real. Only the resonance hybrid, like the rhinoceros, is real.*

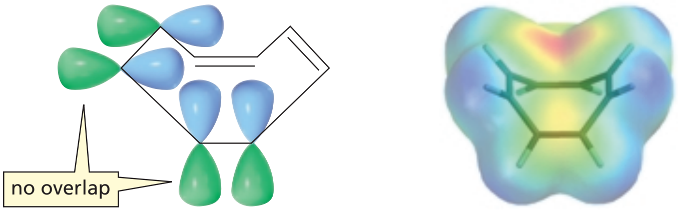


unicorn **resonance contributor** dragon **resonance contributor**



rhinoceros
resonance hybrid

Electron delocalization occurs only if all the atoms sharing the delocalized electrons lie in or close to the same plane, so that their p orbitals can effectively overlap. For example, cyclooctatetraene is not planar, but tub shaped. Because the p orbitals cannot overlap, each pair of π electrons is *localized* between two carbons instead of being *delocalized* over the entire ring of eight carbons.

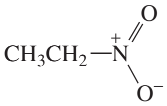


cyclooctatetraene

3-D Molecule:
Cyclooctatetraene

7.4 Drawing Resonance Contributors

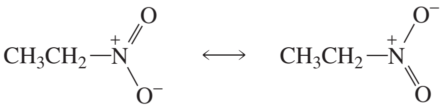
We have seen that an organic compound with delocalized electrons is generally represented as a structure with localized electrons, so that we will know how many π electrons are present in the molecule. For example, nitroethane is represented as having a nitrogen–oxygen double bond and a nitrogen–oxygen single bond.



$CH_3CH_2-\overset{+}{N}(=O)-O^-$

nitroethane

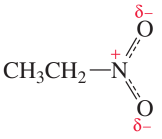
However, the two nitrogen–oxygen bonds in nitroethane are identical; they each have the same bond length. A more accurate description of the molecule's structure is obtained by drawing the two resonance contributors. Both resonance contributors show the compound with a nitrogen–oxygen double bond and a nitrogen–oxygen single bond, but to show that the electrons are delocalized, the double bond in one contributor is the single bond in the other.



resonance contributor   resonance contributor

The resonance hybrid shows that the *p* orbital of nitrogen overlaps the *p* orbital of each oxygen. In other words, the two electrons are shared by three atoms. The resonance hybrid also shows that the two nitrogen–oxygen bonds are identical and that the negative charge is shared by both oxygen atoms. Although the resonance contributors tell us where the formal charges reside in a molecule and give us the approximate bond orders, we need to visualize and mentally average both resonance contributors to appreciate what the actual molecule—the resonance hybrid—looks like.

Delocalized electrons result from a *p* orbital overlapping the *p* orbitals of more than one adjacent atom.



resonance hybrid

Rules for Drawing Resonance Contributors

In drawing resonance contributors, the electrons in one resonance contributor are moved to generate the next resonance contributor. As you draw resonance contributors, keep in mind the following constraints:

1. Only electrons move. The nuclei of the atoms never move.
2. The only electrons that can move are π electrons (electrons in π bonds) and lone-pair electrons.
3. The total number of electrons in the molecule does not change, and neither do the numbers of paired and unpaired electrons.

The electrons can be moved in one of the following ways:

1. Move π electrons toward a positive charge or toward a π bond (Figures 7.2 and 7.3).
2. Move lone-pair electrons toward a π bond (Figure 7.4).
3. Move a single nonbonding electron toward a π bond (Figure 7.5).

▼ **Figure 7.2**
Resonance contributors are obtained by moving π electrons toward a positive charge.

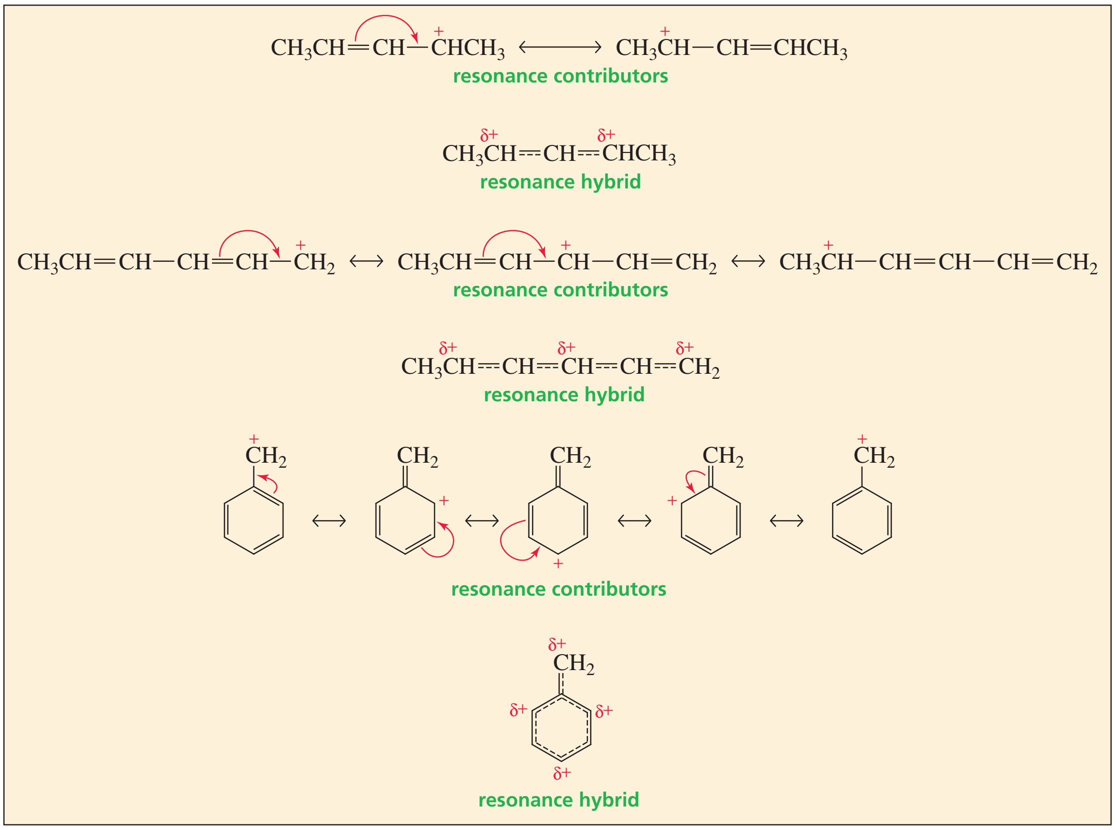
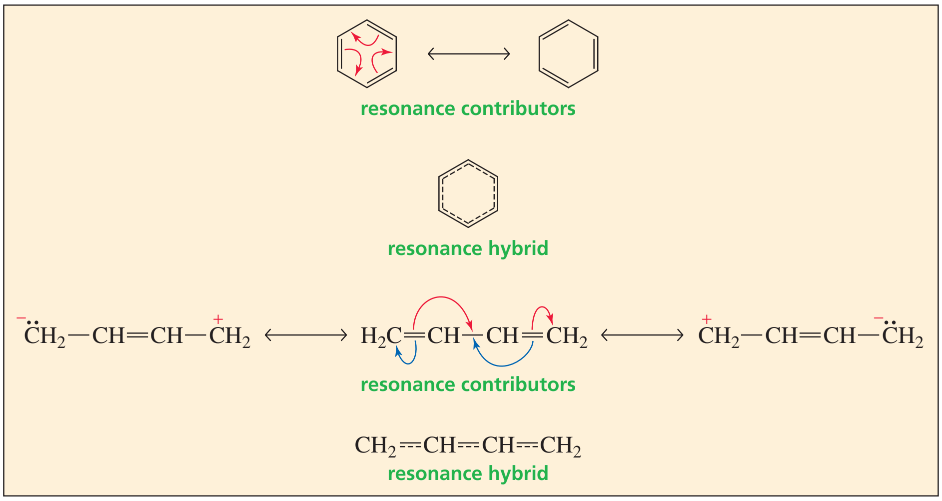


Figure 7.3 ▶
Resonance contributors are obtained by moving π electrons toward a π bond. (In the second example, the red arrows lead to the resonance contributor on the right, and the blue arrows lead to the resonance contributor on the left.)



Notice that in all cases, the electrons are moved toward an sp^2 hybridized atom. Remember that an sp^2 hybridized carbon is either a double-bonded carbon (it can accommodate the new electrons by breaking a π bond) or a carbon that has a positive charge or an unpaired electron (Sections 1.8 and 1.10.) Electrons cannot be moved toward an sp^3 hybridized carbon because it cannot accommodate any more electrons.

Because electrons are neither added to nor removed from the molecule when resonance contributors are drawn, each of the resonance contributors for a particular compound must have the same net charge. If one resonance structure has a net charge of -1, all the others must also have net charges of -1; if one has a net charge of 0, all the others must also have net charges of 0. (A net charge of 0 does not necessarily mean that there is no charge on any of the atoms: A molecule with a positive charge on one atom and a negative charge on another atom has a net charge of 0.)

Radicals can also have delocalized electrons if the unpaired electron is on a carbon that is adjacent to an sp^2 hybridized atom. The arrows in Figure 7.5 are single barbed because they denote the movement of only one electron (Section 3.6).

One way to recognize compounds with delocalized electrons is to compare them with similar compounds in which all the electrons are localized. In the following example, the compound on the left has delocalized electrons because the lone-pair

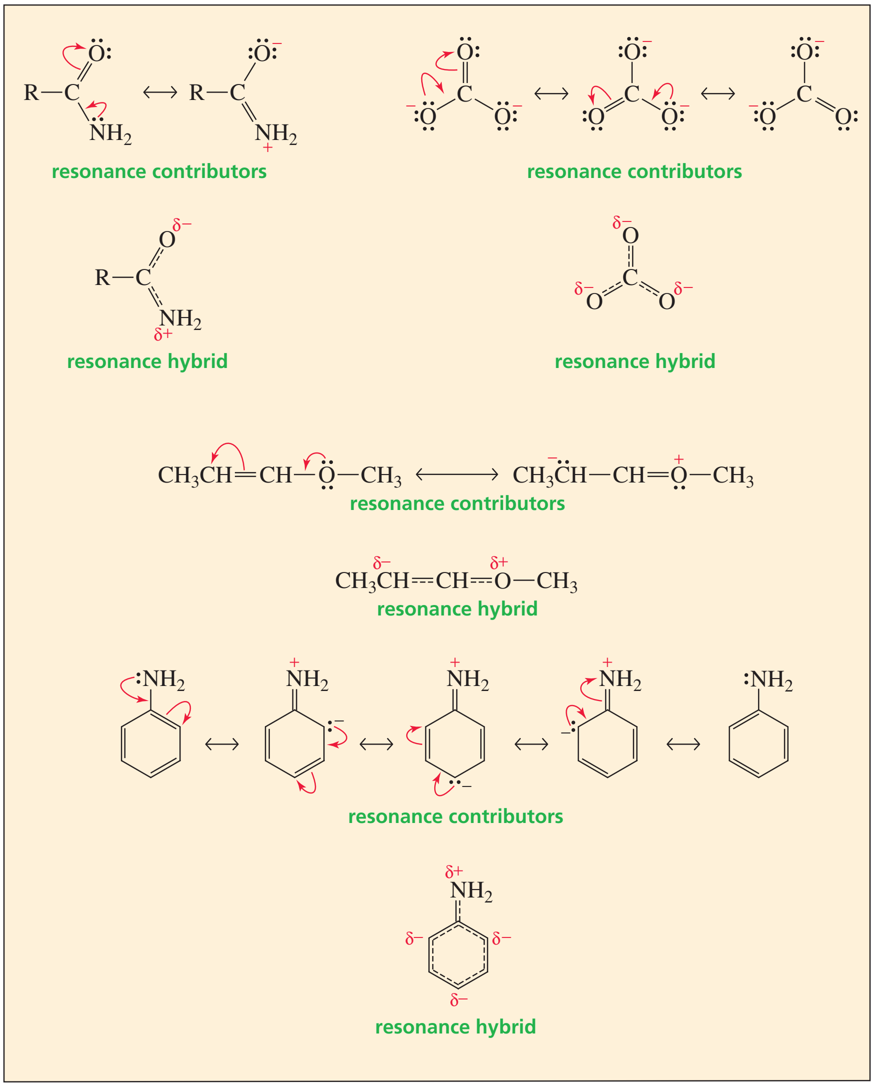


Figure 7.4 Resonance contributors are obtained by moving a lone pair toward a π bond.

Tutorial:
Drawing resonance contributors

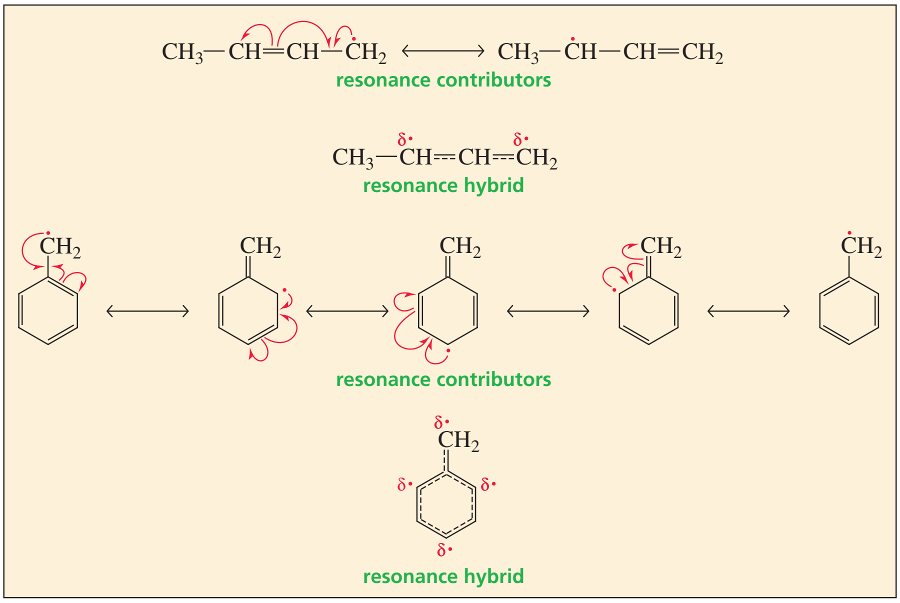
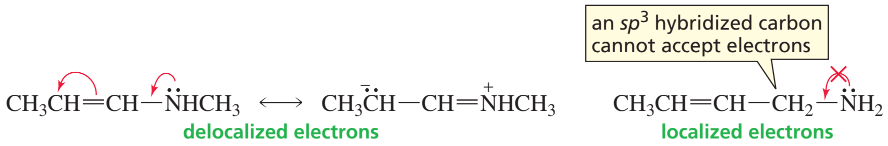


Figure 7.5 ▶
Resonance structures for an allylic radical and for the benzyl radical.

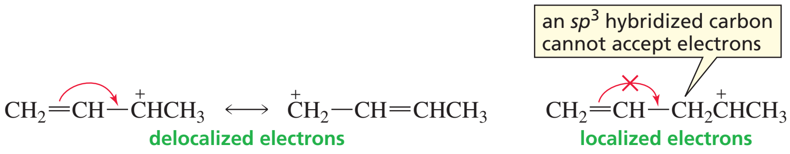
electrons on nitrogen can be shared with the adjacent sp^2 carbon (since the carbon–carbon π bond can be broken):


$CH_3CH{=}CH{-}\ddot{N}HCH_3 \longleftrightarrow CH_3\overset{-}{\ddot{C}}H{-}CH{=}\overset{+}{N}HCH_3 \qquad CH_3CH{=}CH{-}CH_2{-}\ddot{N}H_2$

In contrast, all the electrons in the compound on the right are localized. The lone-pair electrons on nitrogen cannot be shared with the adjacent sp^3 carbon because carbon cannot form five bonds. The octet rule requires that second-row elements be surrounded by no more than eight electrons, so sp^3 hybridized carbons cannot accept electrons. Because an sp^2 hybridized carbon has a π bond that can break, has a positive charge, or has an unpaired electron, it can accept electrons without violating the octet rule.

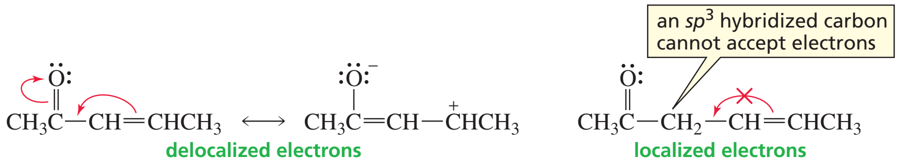
The carbocation shown on the left in the next example has delocalized electrons because the π electrons can move into the empty p orbital of the adjacent sp^2 carbon (Section 1.10). We know that this carbon has an empty p orbital since it has a positive charge.

Tutorial:
Localized and delocalized electrons


$CH_2{=}CH{-}\overset{+}{C}HCH_3 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CHCH_3 \qquad CH_2{=}CH{-}CH_2\overset{+}{C}HCH_3$

The electrons in the carbocation on the right are localized because the π electrons cannot move. The carbon they would move to is sp^3 hybridized, and sp^3 hybridized carbons cannot accept electrons.

The next example shows a ketone with delocalized electrons (left) and a ketone with only localized electrons (right):


$CH_3\overset{\ddot{O}:}{\overset{\|}{C}}{-}CH{=}CHCH_3 \longleftrightarrow CH_3\overset{:\ddot{O}:^-}{\overset{|}{C}}{=}CH{-}\overset{+}{C}HCH_3 \qquad CH_3\overset{\ddot{O}:}{\overset{\|}{C}}{-}CH_2{-}CH{=}CHCH_3$

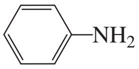
PROBLEM 3◆

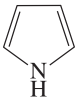
a. Predict the relative bond lengths of the three carbon–oxygen bonds in the carbonate ion (CO_3^{2-}).

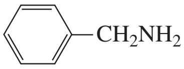
b. What would you expect the charge to be on each oxygen atom?

PROBLEM 4

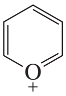
a. Which of the following compounds have delocalized electrons?

1. 

5. 

2. 

6. $CH_3CH{=}CHCH{=}\overset{+}{C}HCH_2$

3. 

7. $CH_3CH_2NHCH_2CH{=}CH_2$

4. $CH_2{=}CHCH_2CH{=}CH_2$

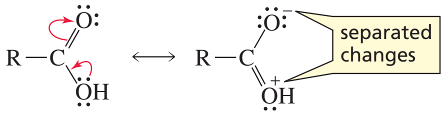
b. Draw the contributing resonance structures for these compounds.

7.5 Predicted Stabilities of Resonance Contributors

All resonance contributors do not necessarily contribute equally to the resonance hybrid. The degree to which each resonance contributor contributes depends on its predicted stability. Because resonance contributors are not real, their stabilities cannot be measured. Therefore, the stabilities of resonance contributors have to be predicted based on molecular features that are found in real molecules. *The greater the predicted stability of the resonance contributor, the more it contributes to the resonance hybrid; and the more it contributes to the resonance hybrid, the more similar the contributor is to the real molecule*. The examples that follow illustrate these points.

The greater the predicted stability of the resonance contributor, the more it contributes to the structure of the resonance hybrid.

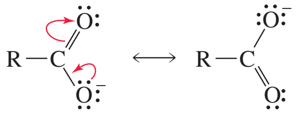
The two resonance contributors for a carboxylic acid are labeled **A** and **B**. Structure **B** has separated charges. A molecule with **separated charges** is a molecule with a positive charge and a negative charge that can be neutralized by the movement of electrons. We can predict that resonance contributors with separated charges are relatively unstable because it takes energy to keep opposite charges separated. Since structure **A** does not have separated charges, it is predicted to have a considerably greater stability. Since structure **A** is predicted to be more stable than structure **B**, structure **A** makes a greater contribution to the resonance hybrid; that is, the resonance hybrid looks more like **A** than like **B**.



A B

a carboxylic acid

The two resonance contributors for a carboxylate ion are shown next.

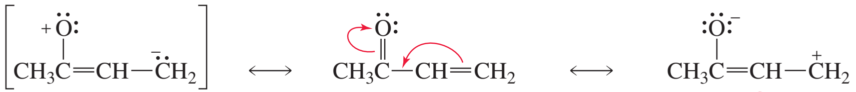


C D

a carboxylate ion

Structures **C** and **D** are predicted to be equally stable and therefore are expected to contribute equally to the resonance hybrid.

When electrons can be moved in more than one direction, they are always moved toward the more electronegative atom. For example, structure **G** in the next example results from moving the π electrons toward oxygen—the most electronegative atom in the molecule. Structure **E** results from moving the π electrons away from oxygen.



$$\left[CH_3\overset{\overset{+\ddot{O}:}{|}}{C}{=}CH{-}\overset{-}{\ddot{C}}H_2\right] \longleftrightarrow CH_3\overset{\overset{\ddot{O}:}{\|}}{C}{-}CH{=}CH_2 \longleftrightarrow CH_3\overset{\overset{:\ddot{O}:^-}{|}}{C}{=}CH{-}\overset{+}{C}H_2$$

E **F** **G**

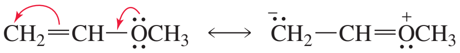
resonance contributor obtained by moving π electrons away from the more electronegative atom

an insignificant resonance contributor

resonance contributor obtained by moving π electrons toward the more electronegative atom

We can predict that structure **G** will make only a small contribution to the resonance hybrid because it has separated charges as well as an atom with an incomplete octet. Structure **E** also has separated charges and an atom with an incomplete octet, but its predicted stability is even less than that of structure **G** because it has a positive charge on the electronegative oxygen. Its contribution to the resonance hybrid is so insignificant that we do not need to include it as one of the resonance contributors. The resonance hybrid, therefore, looks very much like structure **F**.

The only time resonance contributors obtained by moving electrons away from the more electronegative atom should be shown is when that is the only way the electrons can be moved. In other words, movement of the electrons away from the more electronegative atom is better than no movement at all, because electron delocalization makes a molecule more stable (Section 7.6). For example, the only resonance contributor that can be drawn for the following molecule requires movement of the electrons away from oxygen:



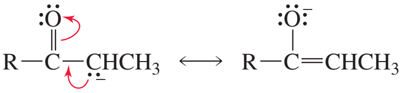
$$CH_2{=}CH{-}\ddot{\underset{..}{O}}CH_3 \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}CH{=}\overset{+}{\underset{..}{O}}CH_3$$

H **I**

Structure **I** is predicted to be relatively unstable because it has separated charges and its most electronegative atom is the atom with the positive charge. Therefore, the structure of the resonance hybrid is similar to structure **H**, with only a small contribution from structure **I**.

Of the two contributing resonance structures for the enolate ion, structure **J** has a negative charge on carbon and structure **K** has a negative charge on oxygen. Oxygen is more electronegative than carbon, so oxygen can accommodate the negative charge better. Consequently, structure **K** is predicted to be more stable than structure **J**. The resonance hybrid, therefore, more closely resembles structure **K**; that is, the resonance hybrid has a greater concentration of negative charge on the oxygen atom than on the carbon atom.

3-D Molecule:
An enolate ion



$$R{-}\overset{\overset{:\ddot{O}}{\|}}{C}{-}\overset{-}{\underset{..}{C}}HCH_3 \longleftrightarrow R{-}\overset{\overset{:\ddot{O}:^-}{|}}{C}{=}CHCH_3$$

J **K**

an enolate ion

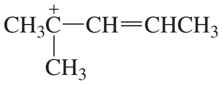
We can summarize the features that decrease the predicted stability of a contributing resonance structure as follows:

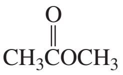
1. an atom with an incomplete octet
2. a negative charge that is not on the most electronegative atom or a positive charge that is not on the least electronegative (most electropositive) atom
3. charge separation

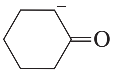
When we compare the relative stabilities of contributing resonance structures, each of which has only one of these features, an atom with an incomplete octet (feature 1) generally makes a structure more unstable than does either feature 2 or feature 3.

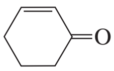
PROBLEM 5 SOLVED

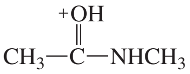
Draw contributing resonance structures for each of the following species, and rank the structures in order of decreasing contribution to the hybrid:

a. 
$CH_3\overset{+}{C}(CH_3)-CH=CHCH_3$

b. 
$CH_3C(=O)OCH_3$

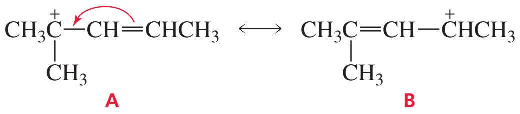
c. 

d. 

e. 
$CH_3-C(=\overset{+}{O}H)-NHCH_3$

f. $CH_3\overset{+}{C}H-CH=CHCH_3$

SOLUTION TO 5a Structure **A** is more stable than structure **B** because the positive charge is on a tertiary carbon in **A** and on a secondary carbon in **B**.


$CH_3\overset{+}{C}(CH_3)-CH=CHCH_3 \longleftrightarrow CH_3C(CH_3)=CH-\overset{+}{C}HCH_3$

PROBLEM 6

Draw the resonance hybrid for each of the species in Problem 5.

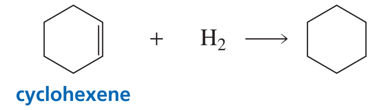
7.6 Resonance Energy

A compound with delocalized electrons is more stable than it would be if all of its electrons were localized. The extra stability a compound gains from having delocalized electrons is called **delocalization energy** or **resonance energy**. **Electron delocalization** gives a compound **resonance**, so saying that a compound is *stabilized by electron delocalization* is the same as saying that it is *stabilized by resonance*. Since the resonance energy tells us how much more stable a compound is as a result of having delocalized electrons, it is frequently called *resonance stabilization*.

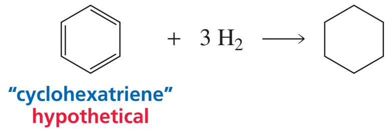
The resonance energy is a measure of how much more stable a compound with delocalized electrons is than it would be if its electrons were localized.

To understand the concept of resonance energy better, let's take a look at the resonance energy of benzene. In other words, let's see how much more stable benzene (with three pairs of delocalized π electrons) is than the unknown, unreal, hypothetical compound "cyclohexatriene" (with three pairs of localized π electrons).

The $\Delta H°$ for the hydrogenation of cyclohexene, a compound with one localized double bond, has been determined experimentally to be -28.6 kcal/mol. We would then expect the $\Delta H°$ for the hydrogenation of "cyclohexatriene," a hypothetical compound with three localized double bonds, to be three times that of cyclohexene; that is, $3 \times (-28.6) = -85.8$ kcal/mol (Section 4.11).

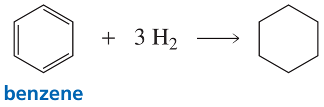


$\Delta H° = -28.6$ kcal/mol (-120 kJ/mol)
experimental



$\Delta H° = -85.8$ kcal/mol (-359 kJ/mol)
calculated

When the $\Delta H°$ for the hydrogenation of benzene was determined experimenally, it was found to be -49.8 kcal/mol, much less than that calculated for hypothetical "cyclohexatriene."



$\Delta H° = -49.8$ kcal/mol (-208 kJ/mol)
experimental

Because the hydrogenation of "cyclohexatriene" and the hydrogenation of benzene both form cyclohexane, the difference in the $\Delta H°$ values can be accounted for only by a difference in the energies of "cyclohexatriene" and benzene. Figure 7.6 shows that benzene must be 36 kcal/mol (or 151 kJ/mole) more stable than "cyclohexatriene" because the experimental $\Delta H°$ for the hydrogenation of benzene is 36 kcal/mol less than that calculated for "cyclohexatriene."

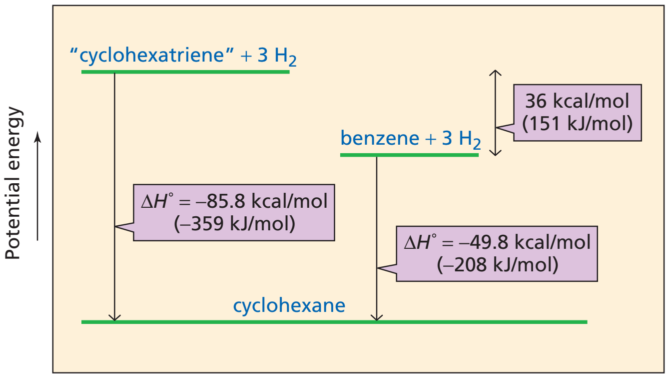


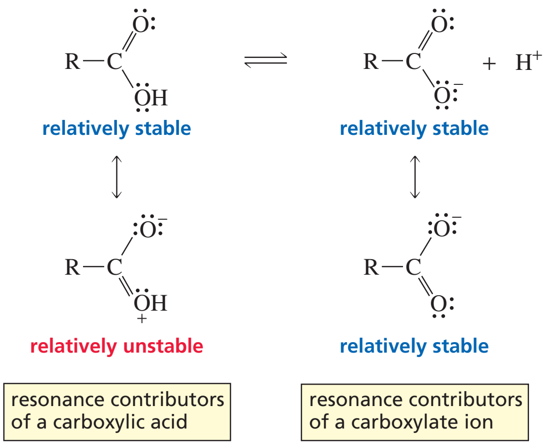
Figure 7.6 ▶
The difference in the energy levels of "cyclohexatriene" + hydrogen versus cyclohexane and the difference in the energy levels of benzene + hydrogen versus cyclohexane.

Because benzene and "cyclohexatriene" have different energies, they must be different compounds. Benzene has six delocalized π electrons, whereas hypothetical "cyclohexatriene" has six localized π electrons. The difference in their energies is the resonance energy of benzene. The resonance energy tells us *how much more stable a compound with delocalized electrons is than it would be if its electrons were localized.* Benzene, with six delocalized π electrons, is 36 kcal/mol more stable than hypothetical "cyclohexatriene," with six localized π electrons. Now we can understand why nineteenth-century chemists, who didn't know about delocalized electrons, were puzzled by benzene's unusual stability (Section 7.1).

A resonance hybrid is more stable than any of its resonance contributors is predicted to be.

Since the ability to delocalize electrons increases the stability of a molecule, we can conclude that *a resonance hybrid is more stable than the predicted stability of any of its resonance contributors.* The resonance energy associated with a compound that has delocalized electrons depends on the number *and* predicted stability of the resonance contributors: *The greater the number of relatively stable resonance* *contributors*, *the greater is the resonance energy*. For example, the resonance energy of a carboxylate ion with two relatively stable resonance contributors is significantly greater than the resonance energy of a carboxylic acid with only one relatively stable resonance contributor.

The greater the number of relatively stable resonance contributors, the greater is the resonance energy.



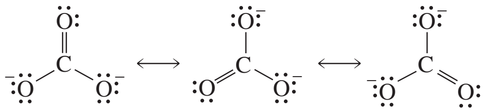
Notice that it is the number of *relatively stable* resonance contributors—not the total number of resonance contributors—that is important in determining the resonance energy. For example, the resonance energy of a carboxylate ion with two relatively stable resonance contributors is greater than the resonance energy of the compound in the following example because even though this compound has three resonance contributors, only one of them is relatively stable:

$$\overset{-}{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2$$

relatively unstable — relatively stable — relatively unstable

The more nearly equivalent the resonance contributors are in structure, *the greater is the resonance energy*. The carbonate dianion is particularly stable because it has three equivalent resonance contributors.

The more nearly equivalent the resonance contributors are in structure, the greater is the resonance energy.

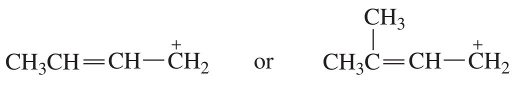


We can now summarize what we know about contributing resonance structures:

1. The greater the predicted stability of a resonance contributor, the more it contributes to the resonance hybrid.
2. The greater the number of relatively stable resonance contributors, the greater is the resonance energy.
3. The more nearly equivalent the resonance contributors, the greater is the resonance energy.

PROBLEM-SOLVING STRATEGY

Which carbocation is more stable?



$$CH_3CH{=}CH{-}\overset{+}{C}H_2 \quad \text{or} \quad CH_3\overset{CH_3}{\overset{|}{C}}{=}CH{-}\overset{+}{C}H_2$$

Start by drawing the resonance contributors for each carbocation.

$CH_3CH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}H{-}CH{=}CH_2 \qquad CH_3\overset{CH_3}{\overset{|}{C}}{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow CH_3\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2$

Then compare the predicted stabilities of the set of resonance contributors for each carbocation.

Each carbocation has two resonance contributors. The positive charge of the carbocation on the left is shared by a primary carbon and a secondary carbon. The positive charge of the carbocation on the right is shared by a primary carbon and a tertiary carbon. Because a tertiary carbon is more stable than a secondary carbon, the carbocation on the right is more stable—it has greater resonance energy.

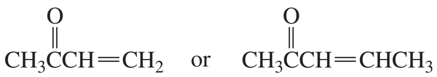
Now continue on to Problem 7.

PROBLEM 7◆

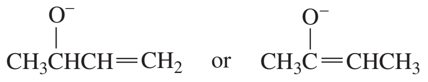
Which species is more stable?

a. 

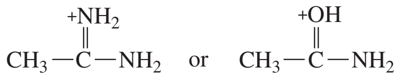
$CH_3CH_2\overset{CH_2}{\overset{\|}{C}}\dot{C}H_2$ or $CH_3CH_2CH{=}CH\dot{C}H_2$

b. 

$CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2$ or $CH_3\overset{O}{\overset{\|}{C}}CH{=}CHCH_3$

c. 

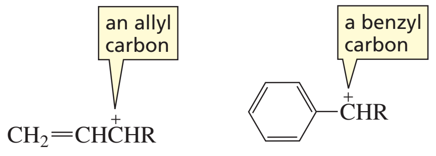
$CH_3\overset{O^-}{\overset{|}{C}}HCH{=}CH_2$ or $CH_3\overset{O^-}{\overset{|}{C}}{=}CHCH_3$

d. 

$CH_3{-}\overset{+NH_2}{\overset{\|}{C}}{-}NH_2$ or $CH_3{-}\overset{+OH}{\overset{\|}{C}}{-}NH_2$

7.7 Stability of Allylic and Benzylic Cations

Allylic and benzylic cations have delocalized electrons, so they are more stable than similarly substituted carbocations with localized electrons. An **allylic cation** is a carbocation with the positive charge on an allylic carbon; an **allylic carbon** is a carbon adjacent to an sp^2 carbon of an alkene. A **benzylic cation** is a carbocation with the positive charge on a benzylic carbon; a **benzylic carbon** is a carbon adjacent to an sp^2 carbon of a benzene ring.

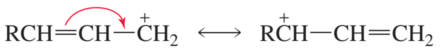


an allylic cation **a benzylic cation**

The *allyl cation* is an unsubstituted allylic cation, and the *benzyl cation* is an unsubstituted benzylic cation.

the allyl cation **the benzyl cation**

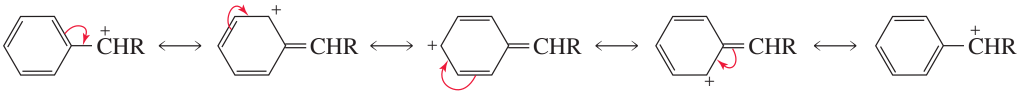
An allylic cation has two resonance contributors. The positive charge is not localized on a single carbon, but is shared by two carbons.



$RCH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow R\overset{+}{C}H{-}CH{=}CH_2$

an allylic cation

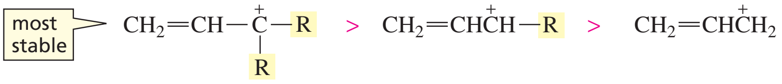
A benzylic cation has five resonance contributors. Notice that the positive charge is shared by four carbons.



a benzylic cation

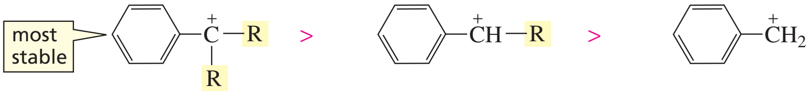
Not all allylic and benzylic cations have the same stability. Just as a tertiary alkyl carbocation is more stable than a secondary alkyl carbocation, a tertiary allylic cation is more stable than a secondary allylic cation, which in turn is more stable than the (primary) allyl cation. Similarly, a tertiary benzylic cation is more stable than a secondary benzylic cation, which is more stable than the (primary) benzyl cation.

relative stabilities



$$\text{most stable} \quad CH_2{=}CH{-}\underset{R}{\overset{+}{C}}{-}R \;>\; CH_2{=}CH\overset{+}{C}H{-}R \;>\; CH_2{=}CH\overset{+}{C}H_2$$

tertiary allylic cation **secondary allylic cation** **allyl cation**

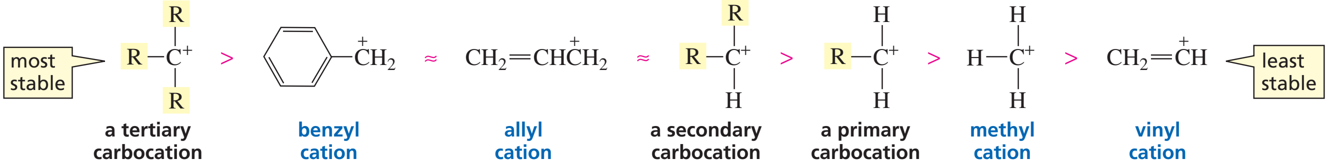


tertiary benzylic cation **secondary benzylic cation** **benzyl cation**

Because the allyl and benzyl cations have delocalized electrons, they are more stable than other primary carbocations. (Indeed, they have about the same stability as secondary alkyl carbocations.) We can add the benzyl and allyl cations to the group of carbocations whose relative stabilities were shown in Sections 4.2 and 6.4.

3-D Molecules:
Allyl cation; Benzyl cation

relative stabilities of carbocations



Notice that it is the *primary* benzyl and the *primary* allyl cations that have about the same stability as *secondary* alkyl carbocations. Secondary benzylic and allylic cations, as well as tertiary benzylic and allylic cations, are even more stable than primary benzyl and allyl cations.

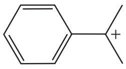
PROBLEM 8◆

Which carbocation in each of the following pairs is more stable?

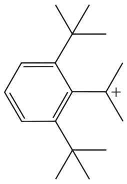
a. $CH_3\overset{+}{O}H_2$ or $CH_3NH\overset{+}{C}H_2$

c. $CH_3OCH_2\overset{+}{C}H_2$ or $CH_3O\overset{+}{C}H_2$

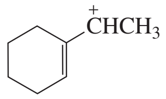
b.



or



d.



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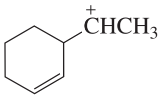
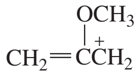


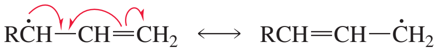
e.



$$CH_2{=}\overset{OCH_3}{\overset{|}{\overset{+}{C}}}H_2 \quad\text{or}\quad CH_3OCH{=}CH\overset{+}{C}H_2$$

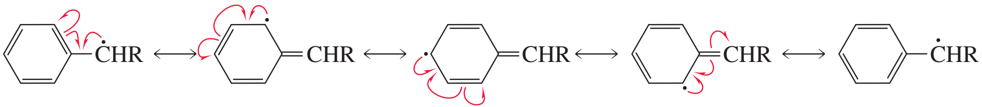
7.8 Stability of Allylic and Benzylic Radicals

An allylic radical has an unpaired electron on an allylic carbon and, like an allylic cation, has two contributing resonance structures.



an allylic radical

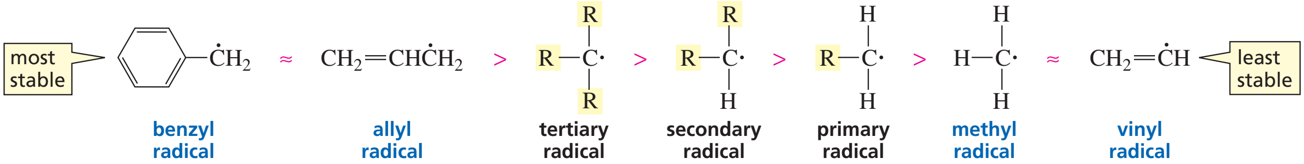
A benzylic radical has an unpaired electron on a benzylic carbon and, like a benzylic cation, has five contributing resonance structures.



a benzylic radical

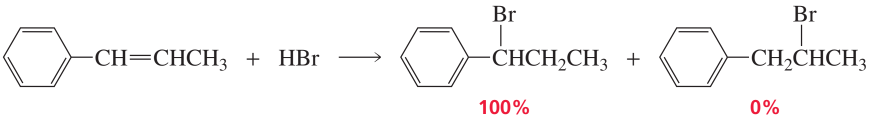
Because of their delocalized electrons, allyl and benzyl radicals are both more stable than other primary radicals. They are even more stable than tertiary radicals.

relative stabilities of radicals



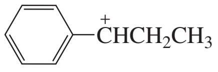
7.9 Some Chemical Consequences of Electron Delocalization

Our ability to predict the correct product of an organic reaction often depends upon recognizing when organic molecules have delocalized electrons. For example, in the following reaction, both sp^2 carbons of the alkene are bonded to the same number of hydrogens:

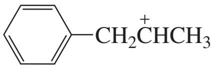


Therefore, the rule that tells us to add the electrophile to the sp^2 carbon bonded to the greater number of hydrogens (or Markovnikov's rule that tells us where to add the proton) predicts that approximately equal amounts of the two addition products will be formed. When the reaction is carried out, however, only one of the products is obtained.

The rules lead us to an incorrect prediction of the reaction product because they do not take electron delocalization into consideration. They presume that both carbocation intermediates are equally stable since they are both secondary carbocations. The rules do not take into account the fact that one intermediate is a secondary alkyl carbocation and the other is a secondary benzylic cation. Because the secondary benzylic cation is stabilized by electron delocalization, it is formed more readily, so only one product is obtained.



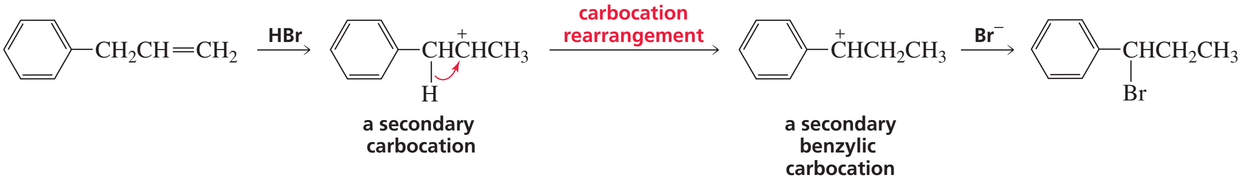
a secondary benzylic cation



a secondary carbocation

This example serves as a warning. Neither the rule indicating which *sp*^{2} carbon the electrophile becomes attached to nor Markovnikov's rule can be used for reactions in which the carbocations can be stabilized by electron delocalization. In such cases, you must look at the relative stabilities of the individual carbocations to predict the product of the reaction.

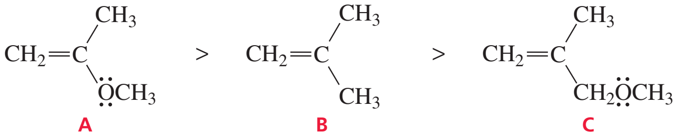
Here is another example of how electron delocalization can affect the outcome of a reaction:



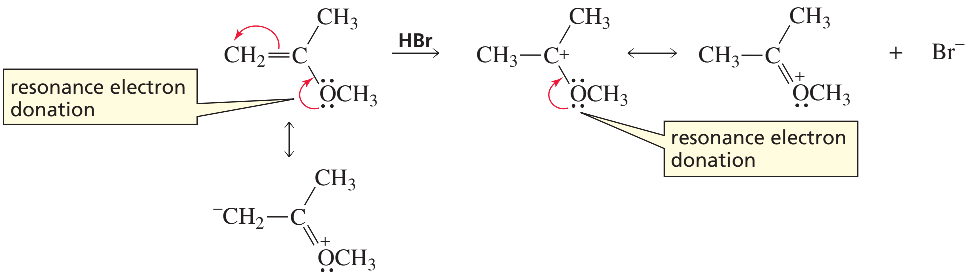
The addition of a proton to the alkene forms a secondary alkyl carbocation. A carbocation rearrangement occurs because a 1,2-hydride shift leads to a more stable secondary benzylic cation (Section 4.6). It is electron delocalization that causes the benzylic secondary cation to be more stable than the initially formed secondary carbocation. Had we neglected electron delocalization, we would not have anticipated the carbocation rearrangement, and we would not have correctly predicted the product of the reaction.

The relative rates at which alkenes **A**, **B**, and **C** undergo an electrophilic addition reaction with a reagent such as HBr illustrate the effect that delocalized electrons can have on the reactivity of a compound.

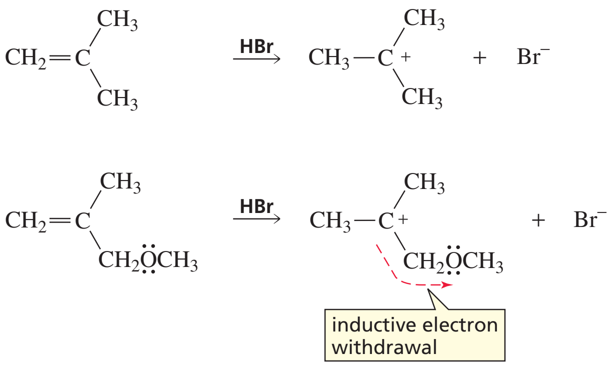
relative reactivities toward addition of HBr



A is the most reactive of the three alkenes. The addition of a proton to the *sp*^{2} carbon bonded to the greater number of hydrogens—recall that this is the rate-limiting step of an electrophilic addition reaction—forms a carbocation intermediate with a positive charge that is shared by carbon and oxygen. Being able to share the positive charge with another atom increases the stability of the carbocation—and, therefore, makes it easier to form. In contrast, the positive charge on the carbocation intermediates formed by **B** and **C** is localized on a single atom.



B reacts with HBr more rapidly than **C** does, because the carbocation formed by **C** is destabilized by the OCH_3 group that withdraws electrons inductively (through the σ bonds) from the positively charged carbon of the carbocation intermediate.

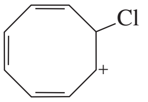


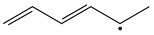
Notice that the OCH_3 group in **C** can only withdraw electrons inductively, whereas the OCH_3 group in **A** is positioned so that in addition to withdrawing electrons inductively, it can donate a lone pair to stabilize the carbocation. This is called **resonance electron donation**. Because stabilization by resonance electron donation outweighs destabilization by inductive electron withdrawal, the overall effect of the OCH_3 group in **A** is stabilization of the carbocation intermediate.

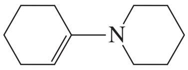
PROBLEM 9 SOLVED

Predict the sites on each of the following compounds where the reaction can occur:

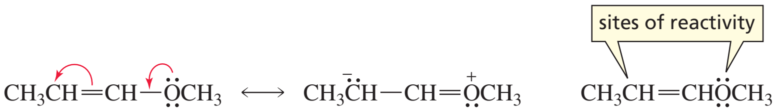
a. $CH_3CH{=}CHOCH_3 + H^+$

b.  + HO^-

c.  + $Br^\bullet$

d.  + H^+

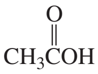
SOLUTION TO 9a The contributing resonance structures show that there are two sites that can be protonated: the lone pair on oxygen and the lone pair on carbon.



resonance contributors

7.10 The Effect of Electron Delocalization on pK_a

We have seen that a carboxylic acid is a much stronger acid than an alcohol because the conjugate base of a carboxylic acid is considerably more stable than the conjugate base of an alcohol (Section 1.19). (Recall that the stronger the acid, the more stable is its conjugate base.) For example, the pK_a of acetic acid is 4.76, whereas the pK_a of ethanol is 15.9.


$CH_3C(=O)OH$

acetic acid
pK_a = 4.76

CH_3CH_2OH
ethanol
pK_a = 15.9

In Section 1.19, you saw that the difference in stability of the two conjugate bases is attributable to two factors. First, the carboxylate ion has a double-bonded oxygen atom in place of two hydrogens of the alkoxide ion. Electron withdrawal by the electronegative oxygen atom stabilizes the ion by decreasing the electron density of the negatively charged oxygen.

Electron withdrawal increases the stability of an anion.

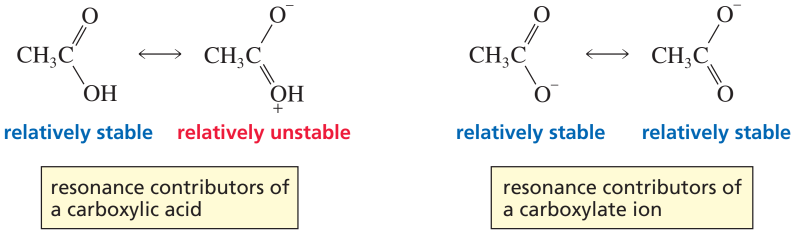
$CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-$

a carboxylate ion

$CH_3CH_2O^-$

an alkoxide ion

The other factor responsible for the increased stability of the carboxylate ion is its *greater resonance energy* relative to that of its conjugate acid. The carboxylate ion has greater resonance energy than a carboxylic acid does, because the ion has two equivalent resonance contributors that are predicted to be relatively stable, whereas the carboxylic acid has only one (Section 7.6). Therefore, loss of a proton from a carboxylic acid is accompanied by an increase in resonance energy—in other words, an increase in stability (Figure 7.7).



In contrast, all the electrons in an alcohol—such as ethanol—and its conjugate base are localized, so loss of a proton from an alcohol is not accompanied by an increase in resonance energy.

$$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$$

ethanol

Phenol, a compound in which an OH group is bonded to an sp^2 carbon of a benzene ring, is a stronger acid than an alcohol such as ethanol or cyclohexanol, compounds

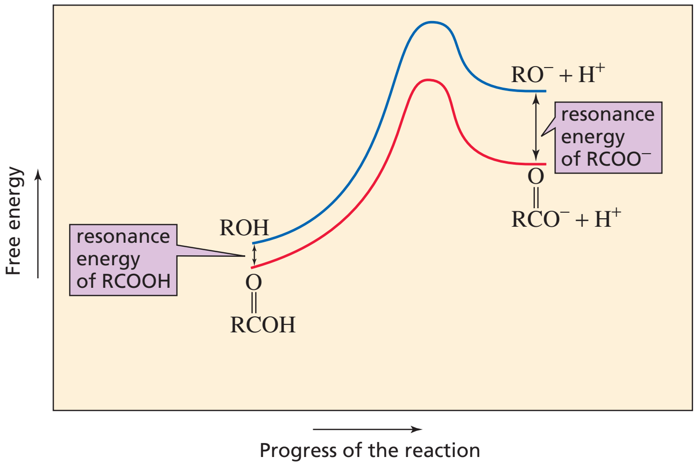
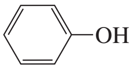
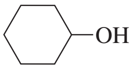


Figure 7.7
One factor that makes a carboxylic acid more acidic than an alcohol is the greater resonance energy of the carboxylate ion, compared with that of the carboxylic acid, which increases the K_a (and therefore decreases the pK_a).

in which an OH group is bonded to an sp^3 carbon. The same factors responsible for the greater acidity of a carboxylic acid compared with an alcohol cause phenol to be more acidic than an alcohol such as cyclohexanol—stablization of phenol's conjugate base by *electron withdrawal* and by *increased resonance energy.*

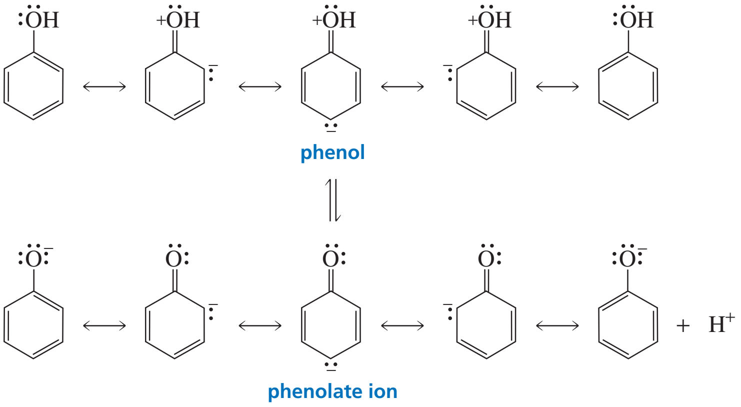
Tutorial:
Acidity and electron delocalization


phenol
pK_a = 10


cyclohexanol
pK_a = 16

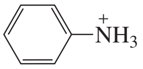
CH_3CH_2OH
ethanol
pK_a = 16

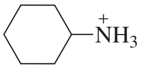
The OH group of phenol is attached to an sp^2 carbon that is more electonegative than the sp^3 carbon to which the OH group of cyclohexanol is attached (Section 6.9). Greater *inductive electron withdrawal* by the sp^2 carbon stabilizes the conjugate base by decreasing the electron density of its negatively charged oxygen. While both phenol and the phenolate ion have delocalized electrons, the resonance energy of the phenolate ion is greater than that of phenol because three of phenol's resonance contributors have separated charges. The loss of a proton from phenol, therefore, is accompanied by an increase in resonance energy. In contrast, neither cyclohexanol nor its conjugate base has delocalized electrons, so loss of a proton is not accompanied by an increase in resonance energy.



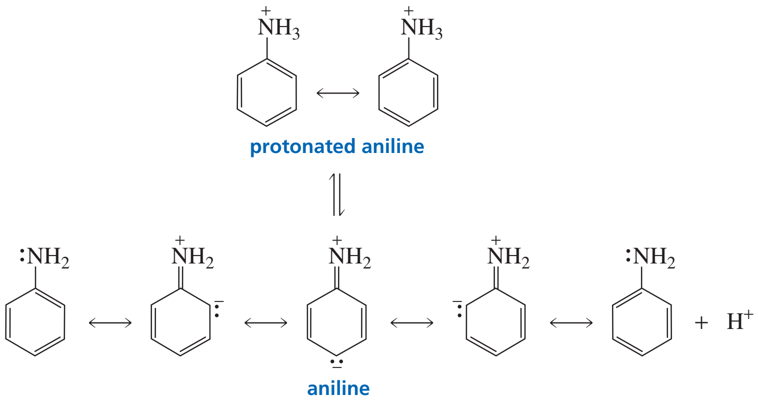
Electron withdrawal from the oxygen in the phenolate ion is not as great as in the carboxylate ion. In addition, the increased resonance energy resulting from loss of a proton is not as great in a phenolate ion as in a carboxylate ion, where the negative charge is shared equally by two oxygens. Phenol, therefore, is a weaker acid than a carboxylic acid.

Again, the same two factors can be invoked to account for why protonated aniline is a stronger acid than protonated cyclohexylamine.

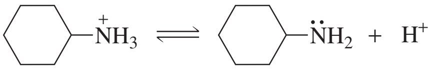

protonated aniline
pK_a = 4.60


protonated cyclohexylamine
pK_a = 11.2

First, the nitrogen atom of aniline is attached to an sp^2 carbon, whereas the nitrogen atom of cyclohexylamine is attached to a less electronegative sp^3 carbon. Second, the nitrogen atom of protonated aniline lacks a lone pair that can be delocalized. When it loses a proton, however, the lone pair that formerly held the proton can be delocalized. Loss of a proton, therefore, is accompanied by an increase in resonance energy.

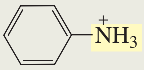
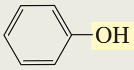


An amine such as cyclohexylamine has no delocalized electrons either in the protonated form or in the unprotonated form, so proton loss is not associated with a change in the amine's resonance energy.



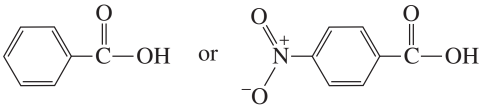
We can now add phenol and protonated aniline to the classes of organic compounds whose approximate pK_a values you should know (Table 7.1). They are also listed inside the back cover for easy reference.

Table 7.1 Approximate pK_a Values

pK_a < 0	pK_a ≈ 5	pK_a ≈ 10	pK_a ≈ 15
$\underset{H}{R\overset{+}{O}H}$	$R\overset{\overset{O}{\Vert}}{C}OH$	$R\overset{+}{N}H_3$	ROH
$R\overset{\overset{+OH}{\Vert}}{C}OH$			H_2O
H_3O^+			

PROBLEM 10 SOLVED

Which of the following would you predict to be the stronger acid?



SOLUTION The nitro-substituted compound is the stronger acid because the nitro substituent can withdraw electrons inductively (through the σ bonds) and it can withdraw electrons by resonance (through the π bonds). We have seen that electron-withdrawing substituents increase the acidity of a compound by stabilizing its conjugate base.