

Objective 3: Draw resonance structures, use curved arrows, determine extent of delocalization. Identify major/minor contributor.

### Quiz Practice problems

#### Key ideas:

The Lewis structure model represents the bonding in most molecules very well, as long as electrons are localized (shared between two atoms). But if electrons are delocalized (shared between three or more atoms), a Lewis structure does not accurately represent the bonding in a compound. Two or more resonance structures are used to show electron delocalization. Use double sided arrow to represent resonance structures.

Use curved arrows to show how electrons are delocalized between atoms in resonance structures (which electrons are delocalized and which atoms are sharing electrons):

Pi bond breaks to form pi bond on adjacent bond.

Pi bond breaks to form lone pair on atom.

Lone pair on atom can form pi bond.

Resonance structures can be equivalent (same stability) or one resonance structure is the major contributor (more stable) and another resonance structure(s) is/are the minor contributor (less stable). See formal charge rules for stability.

#### Skills:

Use curved arrows to show how electrons are delocalized between atoms in resonance structures. In other words, given one resonance structure, use curved arrows to draw another resonance structure. (See Alchemie Mechanisms app Homework.)

Determine extent of delocalization, i.e., over how many atoms are sharing the pi electrons or lone pairs or both.

Identify the major and minor resonance structure contributors using formal charge rules.

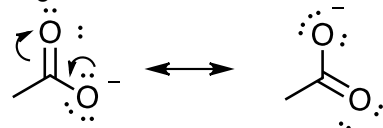
1. Experiments show the acetate ion ( $\text{CH}_3\text{COO}^-$ ) has two carbon-oxygen bonds of the same length.

The Lewis structure of acetate shows a C-O single bond and a C=O double bond, which are not the same length, and does not accurately represent the bonding in acetate.

a. Draw a resonance structure to show the two carbon-oxygen bonds have the same length.

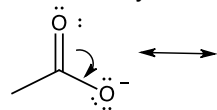
b. Use curved arrows to go from one resonance structure to the second resonance structure.

In general, start the curved arrow at a lone pair or pi bond.



Note in this case, the arrow starts at the lone pair on the O with a (-) charge to give the second resonance structure.

If you start the curved arrow at the pi bond, you will not get the second resonance structure. Check the octet rule to confirm why this does not work.

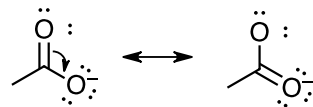


c. How many atoms are electrons delocalized (shared)? Answer: 3 (a lone pair and pi electrons are shared between the oxygen, carbon, and oxygen).

d. Which resonance structure is the major contributor (more stable)? Apply formal charge rules. Answer: Both or neither. Each resonance structure has the same stability.

#### Answers:

b. On resonance structure on the right, each O does not fit the octet rule.



c. 3 atoms: compare the two resonance structures - one lone pair and one pi bond are delocalized (shared) between the O, C, and other O.

d. On each resonance structure,

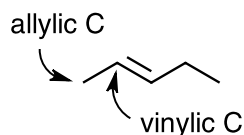
formal charge on C bonded to O =  $4 - 4 - 0 = 0$ ,

formal charge on O double bonded to C =  $6 - 2 - 4 = 0$

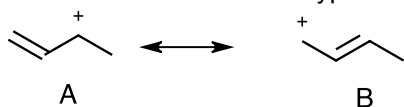
formal charge on O single bonded to C =  $6 - 1 - 6 = -1$ .

So the two resonance structures are equivalent.

2. An alkene is shown below. The C in a C=C bond is called the vinylic carbon. The C adjacent to the vinylic carbon is called the allylic carbon. Circle the other vinylic C. Box the other allylic C.



An allylic carbocation is shown below. Experiments show the C1-C2 bond is longer than a typical C=C bond and the C2-C3 bond is shorter than a typical C-C bond.



- Draw in the H's and lone pairs.
- Confirm the carbon with a (+) charge by calculating the formal charge at this atom.
- Use curved arrows to go from one resonance structure to the second resonance structure. (At which atom or bond should you start a curved arrow?)
- How many atoms are electrons delocalized (shared)?
- Which resonance structure is the major contributor (more stable)? Hint: Apply formal charge rules.

Answer: resonance structure A is the major contributor. A 2° allylic carbocation (Structure A) is more stable than a 1° allylic carbocation (Structure B).

**Note:** Carbocation stability: 3° C<sup>+</sup> > 2° C<sup>+</sup> > 1° C<sup>+</sup>.

A 3° C<sup>+</sup> (tertiary carbocation) is a carbocation with three carbons bonded to it.

A 2° C<sup>+</sup> (secondary carbocation) is a carbocation with two carbons bonded to it.

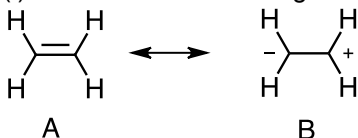
A 1° C<sup>+</sup> (primary carbocation) is a carbocation with one or zero carbons bonded to it.

Allylic C<sup>+</sup> is more stable than a "regular" C<sup>+</sup>, e.g., allylic 2° C<sup>+</sup> is more stable than a 2° C<sup>+</sup>.

Carbocations are intermediates in some types of substitution, elimination, and addition reactions (which we will look at later in Chem 12A).

f. Ethylene (H<sub>2</sub>C=CH<sub>2</sub>) is an important starting material to make many organic compounds.

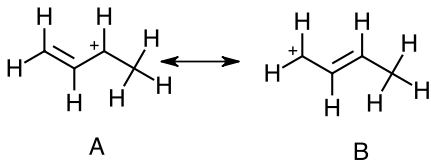
(i) Use curved arrows to go from Structure A to Structure B. Show lone pairs as needed.



(ii) Are Structures A and B resonance structures? Give reasons.

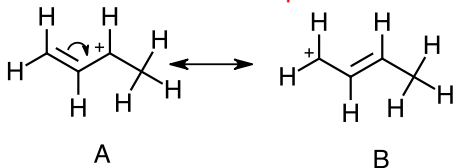
**Answers:**

a.



b. formal charge on C with (+) charge (carbocation) = 4 - 3 - 0 = 1

c. Start curved arrow at pi bond.



d. 3 atoms: compare the two resonance structures - one pi bond and (+) charge are delocalized (shared) between the vinylic carbons and allylic carbocation.

e. On each resonance structure,

formal charge on each vinylic C = 4 - 4 - 0 = 0

formal charge on allylic carbocation = 4 - 3 - 0 = 1

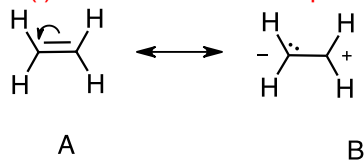
formal charge on other C = 4 - 4 - 0 = 0

On resonance structure A, (+) charge is on secondary (2°) allylic carbocation (secondary because there are two carbons bonded to the carbocation).

On resonance structure B, (+) charge is on primary (1°) allylic carbocation (primary because there is one carbon bonded to the carbocation).

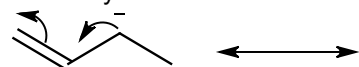
Secondary ( $2^\circ$ ) allylic carbocation is more stable (lower in energy) than the primary ( $1^\circ$ ) allylic carbocation so A is the major resonance contributor.

f. (i) Curved arrow shows pi bond forms a lone pair.



(ii) Resonance structures show delocalized electrons (sharing of electrons between 3 or more atoms). In Structures A and B, the pi bond and lone pair and charges are shared between 2 carbons ==> NOT resonance structures.

3. An allylic carbanion is shown below.



a. Draw in the H's and lone pairs.

b. Confirm the carbon with a (-) charge by calculating the formal charge at this atom.

c. (i) The curved arrows on the structure are shown. (Note: the arrow on the right starts from a lone pair, which is not shown. The arrow on the left ends with a lone pair.) Draw the 2<sup>nd</sup> resonance structure.

(ii) If you start the curved arrow at the pi bond and go right, you will not get the second resonance structure. Check the octet rule to confirm why this does not work.

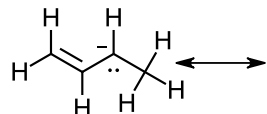
d. How many atoms are electrons delocalized (shared)?

e. Which resonance structure is the major contributor (more stable)? Apply formal charge rules.

Carbanion stability follows the same order as carbocation stability.

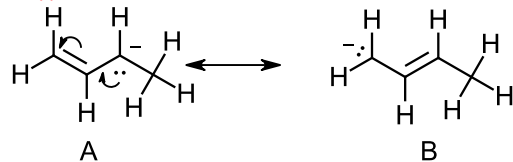
Answers:

a.

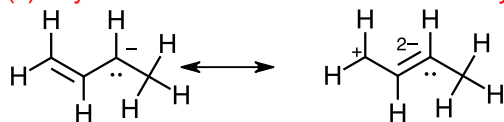


b. formal charge on C with a (-) charge (carbanion) =  $4 - 3 - 2 = -1$

c. (i)



(ii) Allylic carbanion has 6 electrons. Vinylic C has 10 electrons and -2 charge (FC =  $4 - 4 - 2 = -2$ ).

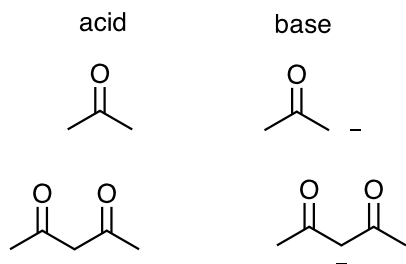


d. 3 atoms: compare the two resonance structures - one pi bond and lone pair and (-) charge are delocalized (shared) between the vinylic carbons and allylic carbanion.

e. Resonance structure A is more stable than B. A has a secondary ( $2^\circ$ ) allylic carbanion that is more stable than the primary ( $1^\circ$ ) allylic carbanion in B.

4. We will look at organic acids and bases in Chem 12A. A strong acid has a weak conjugate base and a weak acid has a strong conjugate base (you remember this from Chem 1B). A strong base is more stable than a weak base. Resonance structures can tell us about the stability of a base.

Two acids and their conjugate bases are shown below.

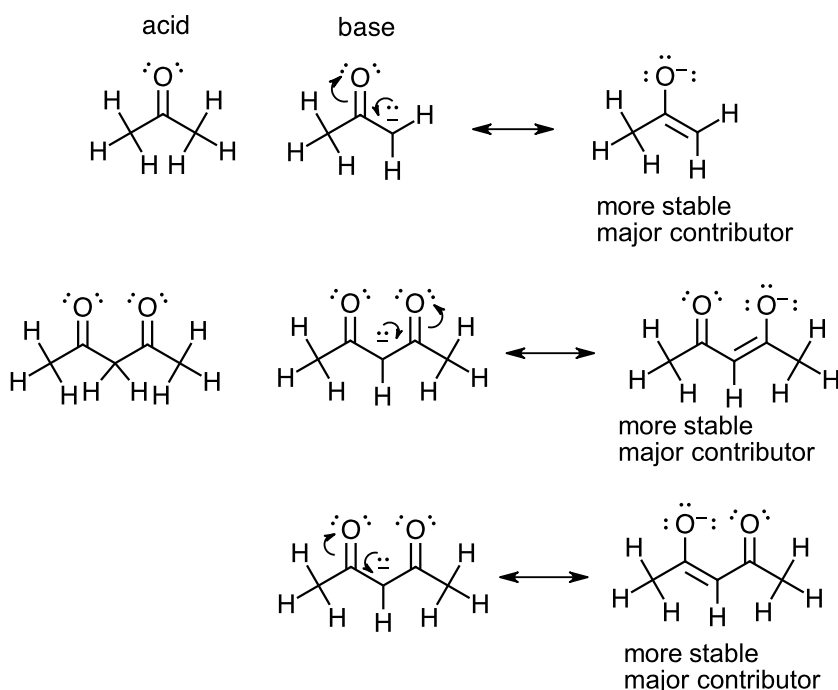


- For each base, draw in the H's and lone pairs.
- Draw resonance structures for each base. Use curved arrows to go from one resonance structure to another. (Hint: two resonance structures for the first base. More than two resonance structures for the second base.)
- For each base, which resonance structure is the major contributor (more stable)? Give reasons.
- Based on your answer to (b), which acid is stronger?

Answers:

a and b and c.

For c, each resonance structure has an atom with a formal charge = -1. The more electronegative atom with the (-) formal charge is more stable – in this case O is more electronegative than C so the resonance structure with the -1 formal charge on the O is more stable than the resonance structure with the -1 formal charge on C.



d. General rule for stability – more resonance structures ==> more stable.

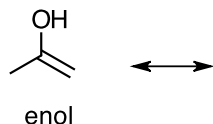
Reason – more resonance structures indicates more delocalization (electrons are shared between more atoms).

So the base with two O's is more stable.

The more stable base is produced from the stronger acid ==> this means the acid with two O's (2,4-pentanedione) is stronger than acetone.

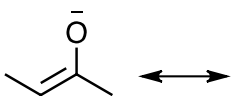
You'll see this compound again in Chem 12B.

5. We will look at how an alkyne forms an enol, which forms an aldehyde or ketone later in Chem 12A.



- (i) Draw in the H's and lone pairs in the enol.
- (ii) Draw the resonance structure. Use curved arrows to go from one resonance structure to another.
- (iii) Which resonance structure is the major contributor (more stable)? Give reasons.

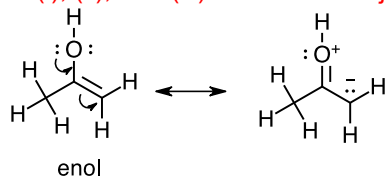
b. An enolate ion is shown below.



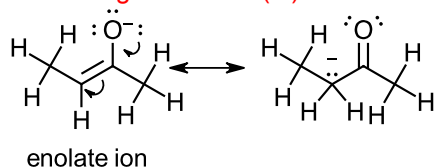
- (i) Draw in the H's and lone pairs.  
 (ii) Draw the resonance structure. Use curved arrows to go from one resonance structure to another.  
 (iii) Which resonance structure is the major contributor (more stable)? Give reasons.

Answers:

a. (i), (ii), and (iii) enol is the major contributor (more stable) – lower formal charges.

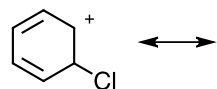


b. a. (i), (ii), and (iii) enolate ion is the major contributor (more stable) because -1 formal charge is on the more electronegative atom (O).



You'll see this compound again in Chem 12B.

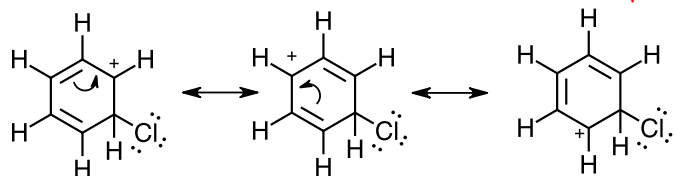
6. We will look at how aromatic compounds undergo substitution reactions in Chem 12B. A reaction intermediate is shown below.



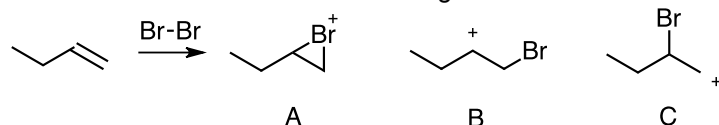
- a. Draw in the H's and lone pairs.  
 b. Draw the resonance structures (there are at least three). Use curved arrows to go from one resonance structure to another.  
 c. Which resonance structure is the major contributor (more stable)? Give reasons.

Answers:

a and b and c. The three resonance structures are equivalent. Each structure is a secondary (2°) allylic carbocation.



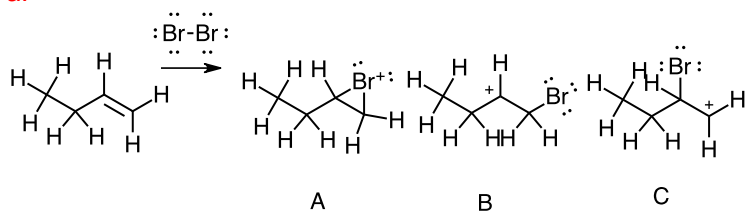
7. We will look at how alkenes undergo an addition reaction with Br<sub>2</sub> later in Chem 12A. Consider Structures A, B, and C.



- a. Draw in the H's and lone pairs in A, B, and C.  
 b. Explain why A and B and C are not resonance structures.  
 c. Are A and B the same compound, different compounds, or isomers?

Answers:

a.



b. A, B, and C are not resonance structures because the sigma bonds are different.

Resonance structures show sharing (delocalization) of pi bonds and lone pairs.  
c. A and B are isomers – same chemical formula, different bonding.