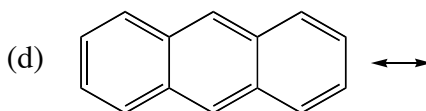
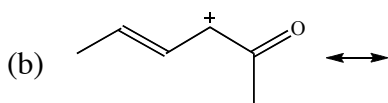
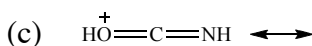
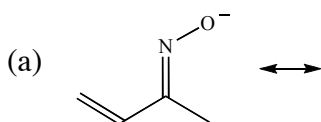


- Complete this sentence: Resonance can have a significant impact on molecular structure and stability because electrons are _____ and _____ by resonance.
- In lecture we explored four important patterns and one rare pattern of electron pair shift in resonance contributors. With these patterns in mind, draw at least one more resonance contributor in each case. Include all lone pairs. Name the electron pair shift pattern in each case.



- List the five resonance contributor preference rules. Give an example of each. Which of these preference rules is most influential?
- Label the most significant resonance contributor for each molecule in CFQ 5. Briefly explain your reasoning.
- Draw the resonance hybrid for each molecule in CFQ 5.
- Of all of the molecular representations in CFQs 5, 7, and 8 which is the best representation of an actual molecular structure?

Concept Focus Question Solutions

- Illustrated definitions can be found at the Illustrated Glossary of Organic Chemistry available at the course web site.

Resonance: A situation in which a molecule can be represented by two or more valid Lewis structures.

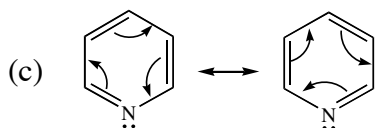
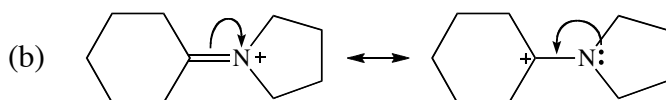
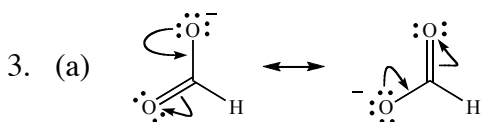
Resonance contributor: One of the Lewis structures that contributes to resonance.

Resonance hybrid: A weighted average of resonance contributors depicting the true electronic structure of a molecule.

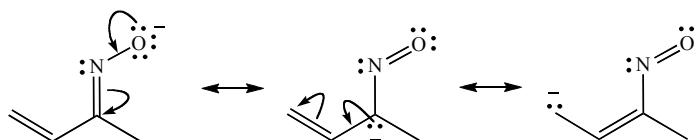
Curved arrow: A notation used to indicate the relocation of electrons. The tail of the arrow indicates the source of the electrons, and the head of the arrow indicates their destination.

Electron delocalization: Distribution of electron density beyond a fixed place such as a lone pair or covalent bond.

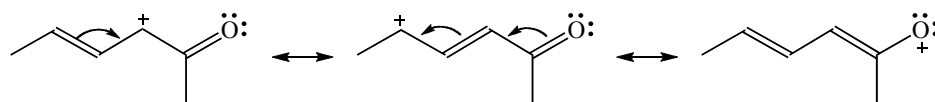
2. (a) Resonance contributors have no physical reality or lifetime, and do not interconvert. Equilibrium structures have a definite (and sometimes very small) lifetime, and do interconvert.
- (b) Resonance contributors are separated by an arrow that has a single shaft and two double-barbed heads: \longleftrightarrow . Structures in equilibrium are separated by an arrow with two parallel shafts, each with a single-barbed head, pointing in opposite directions: \rightleftharpoons .



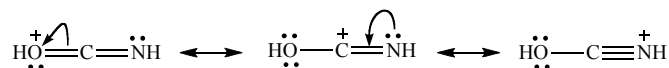
4. Resonance can have a significant impact on molecular structure and stability because electrons are **delocalized** and **stabilized** by resonance.
5. (a) Pattern = Lone pair and pi bond switch places.



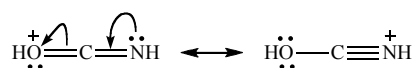
- (b) Pattern = Open octet and pi bond switch places.



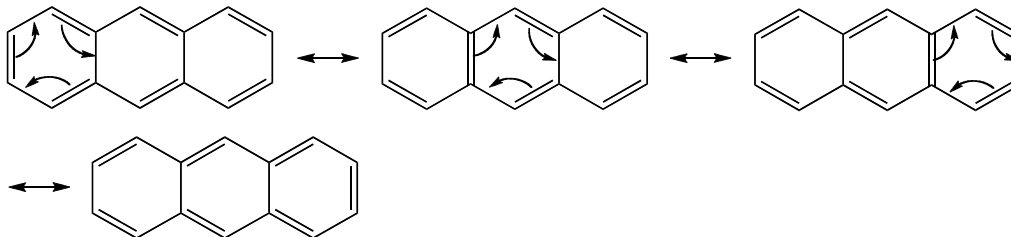
- (c) Pattern = Pi bond becomes lone pair and open octet (and reverse).



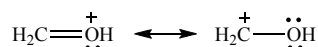
Or: lone pair and pi bond switch places.



(d) Aromatic pi bonds circulate.



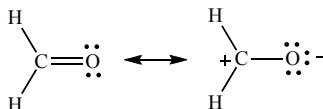
6. **Rule 1:** The most important contributor has the maximum number of atoms with full octets.



More important Less important
All octets full *One open octet*

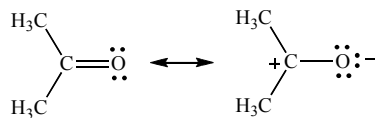
This preference rule is more influential than all other preference rules, which have no particular order of importance.

Rule 2: The most significant contributor has the maximum number of covalent bonds.



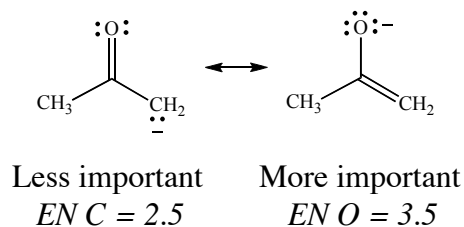
More important Less important
Four bonds *Three bonds*

Rule 3: The most significant contributor has the least number of formal charges.

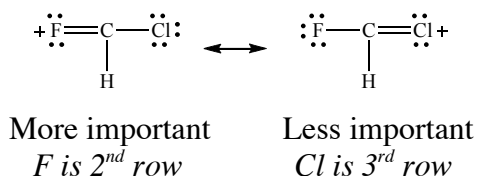


More important Less important
No FC *Two FC*

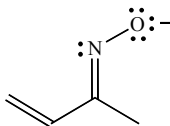
Rule 4: If a resonance contributor must have formal charge, the most important contributor has these charge(s) on the atoms most willing to accommodate them. Negative charges are best on more electronegative atoms; positive charges are best on less electronegative atoms.



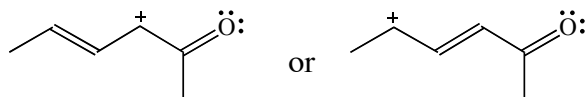
Rule 5: Resonance interaction (i.e., pi bond) is strongest between atoms in the same row of the periodic table. Usually CNOF. Usually outweighs electronegativity considerations.



7. (a) All atoms have full octets. The contributors differ by location of the negative charge, which is best accommodated on the most electronegative atom. Therefore the most significant resonance contributor is

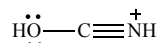


- (b) None of these contributors has a full octet on every atom. The positive charge is best accommodated on the least electronegative atom so the most significant contributor is

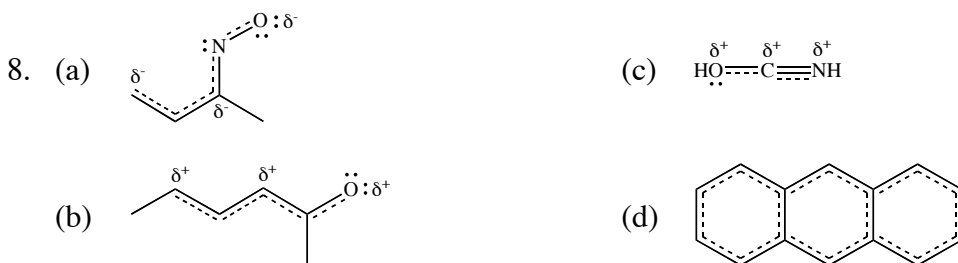


Later in this course we will learn more about structures in which carbon bears a positive charge (called carbocations), and how to choose between these two contributors.

- (c) The contributor with a formal positive charge on carbon has an open octet on carbon. All octets are full on the other contributors. The positive charge is best accommodated on the least electronegative atom so the most significant resonance contributor is:



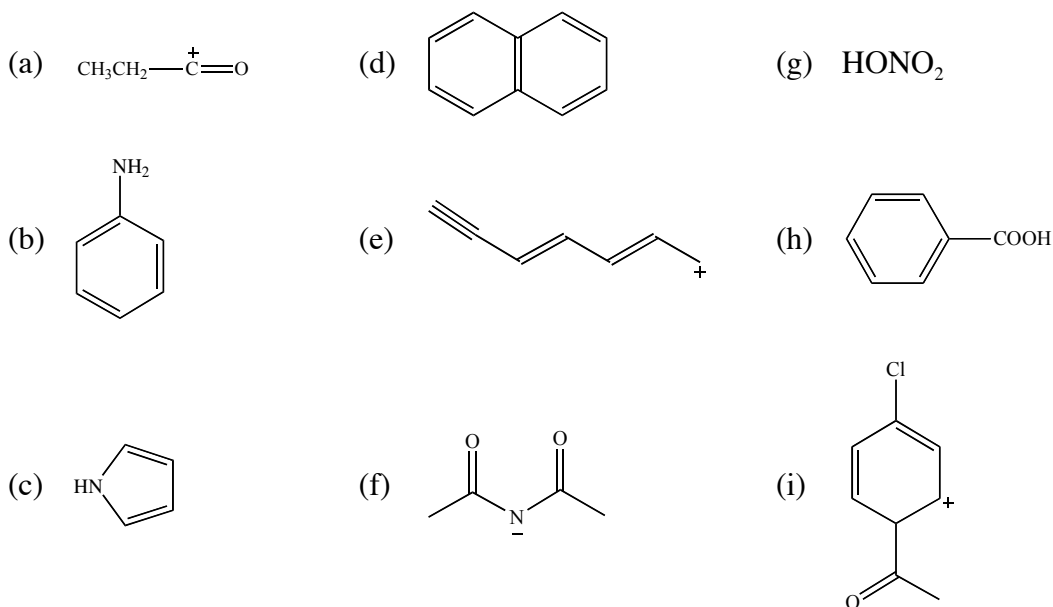
- (d) All of the contributors have full octets on each atom, the same number of covalent bonds, and no formal charges. The contributors are all of equal significance.



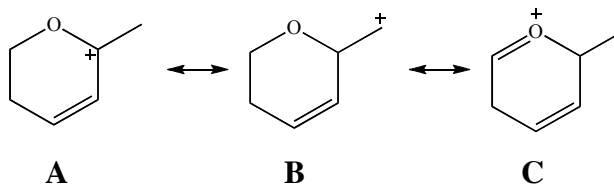
9. For any molecule that has resonance, the best (the most realistic) representation of its structure is the resonance hybrid.

OWLS Problems

1. In each case, draw at least two more significant resonance contributors, including the most important contributor. Include all curved arrows, lone pairs, and formal charges. Also draw the corresponding resonance hybrids.



2. Resonance has wide-ranging effects in organic chemistry. Drawing resonance contributors and hybrids is an important skill that is frequently troublesome. You must be able to draw these structures quickly and accurately. This problem will help you recognize and overcome some common resonance errors.

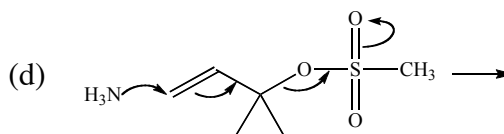
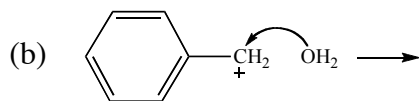
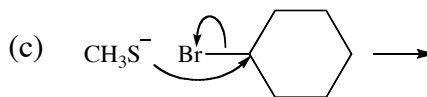
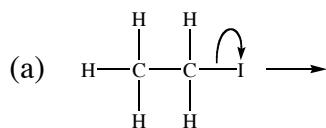


(a) Structure **A** is correct. Explain what is wrong (if anything) with resonance contributors **B** and **C**.

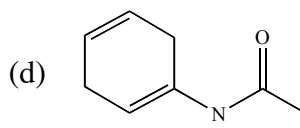
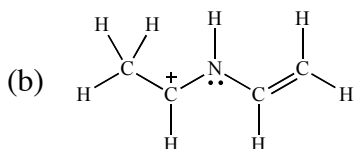
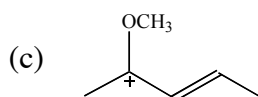
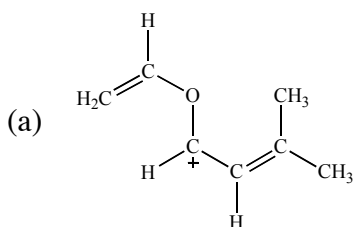
- (b) Draw the other two significant resonance contributors, as well as the resonance hybrid, for cation **A**.

Practice Problems

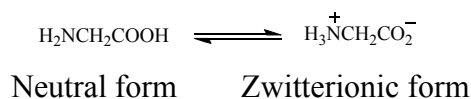
1. Draw the new structures based on the curved arrows. Include all lone pairs and formal charges for all reactants and products.



2. Draw the three most significant resonance contributors for each molecule, including all lone pairs and formal charges. (For an added challenge, see if you can do this without drawing any curved arrows.) Label the most significant contributor. Draw each resonance hybrid.

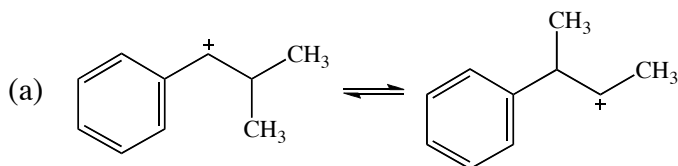


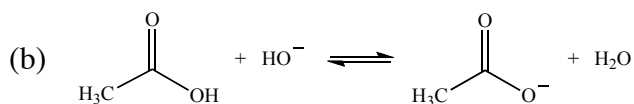
3. How do you answer a classmate who asks you “How many resonance contributors do I draw? How many contributors contribute to the hybrid?”
4. Glycine is the simplest amino acid, a group of small molecules that are the basic building blocks of proteins. In aqueous solution all amino acids are in equilibrium with their zwitterionic isomers. An incomplete representation of this equilibrium for glycine is shown.



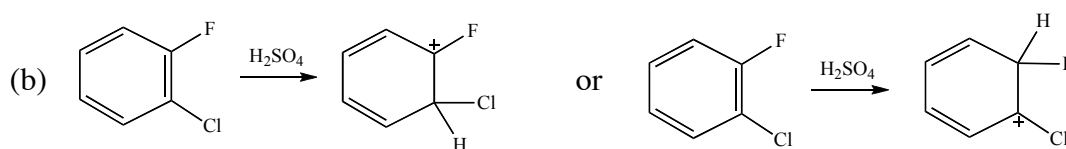
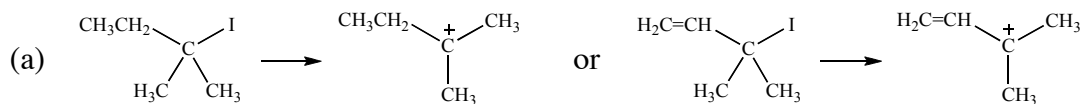
- (a) Draw three resonance contributors for both the neutral and zwitterionic forms of glycine. Also draw the resonance hybrids.

- (b) Which resonance contributor is most significant?
5. Resonance is a significant reason why sulfuric acid is such a strong acid.
- Draw the resonance contributors for sulfuric acid (H_2SO_4) and its conjugate base bisulfate ion (HOSO_3^-) that do not violate any resonance contributor preference rules (i.e., only the most significant contributors).
 - How does sulfur enhance or inhibit the resonance stabilization of these molecules?
 - Based on the resonance of sulfuric acid and bisulfate ion, suggest a reason why sulfuric acid is such a strong acid (i.e., why sulfuric acid readily gives up a hydrogen atom to become bisulfate ion.)
6. Resonance has a great deal of influence on the structure and reactivity of carbonyl-containing functional groups that are similar to carboxylic acids.
- Draw three resonance contributors for these molecules: HCOOH (a carboxylic acid), HCOOCH_3 (an ester), HCONH_2 (an amide), HCOCl (an acid chloride), and HCOSCH_3 (a thioester).
 - What is the most significant resonance contributor for each of these molecules?
 - Draw generic resonance contributors and the hybrid for each of these molecules using HCOX , where $\text{X} = \text{OH}, \text{OCH}_3, \text{NH}_2, \text{Cl}, \text{or } \text{SCH}_3$. What can we say about resonance among similar functional groups?
 - The barrier to rotation around the C-X bond of each of these functional groups is higher than a normal sigma bond. Explain.
 - Which molecule has the highest barrier to rotation around the C-X bond?
7. The barrier to rotation around a bond is defined as the energy difference between the lowest and highest energy conformations. The barrier to rotation around the C-O bond of methanol ($\text{H}_3\text{C-OH}$) is rather low ($1.1 \text{ kcal mol}^{-1}$), whereas the barrier to rotation around the C-O bond in the corresponding cation $^+\text{H}_2\text{C-OH}$ is much higher (about 18 kcal mol^{-1}). Why is the barrier to rotation for the cation so much higher than the barrier to rotation for methanol?
8. Resonance can influence many aspects of molecular structure.
- Why are the carbon-carbon bonds of benzene shorter than the carbon-carbon bonds of cyclohexane, but longer than the carbon-carbon bond of ethylene?
 - Why is the C-O bond of phenol less polar than the C-O bond of cyclohexanol?
9. Resonance can influence many aspects of chemical reactivity. For the following equilibria, predict which side is favored (i.e., $K_{eq} > 1$ or $K_{eq} < 1$), and provide an explanation.



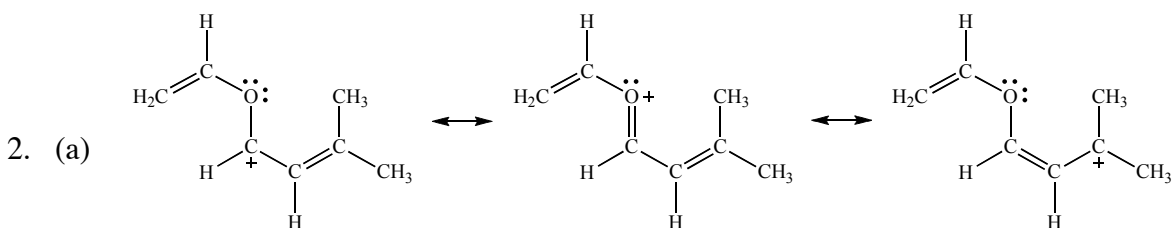
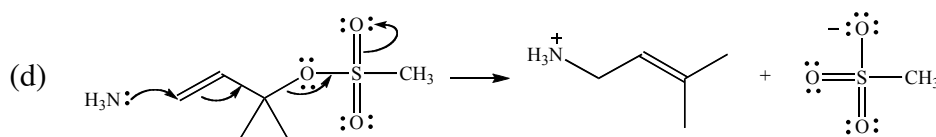
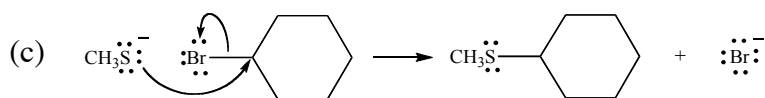
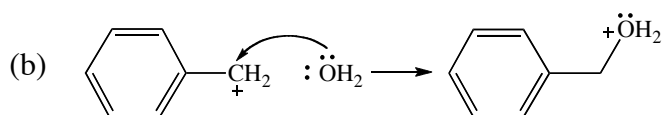
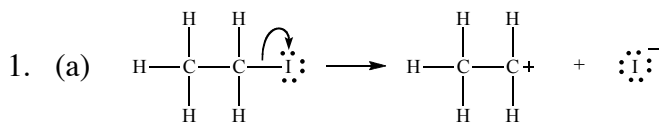


10. Resonance can also influence the rate at which reactions occur. For example, if two reactions are very similar but give different products, the reaction that produces the more stable product is probably faster. Based on this concept, select the faster reaction of each pair and briefly explain your choice. Include all significant resonance contributors in your explanation.

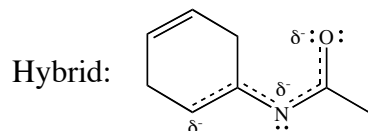
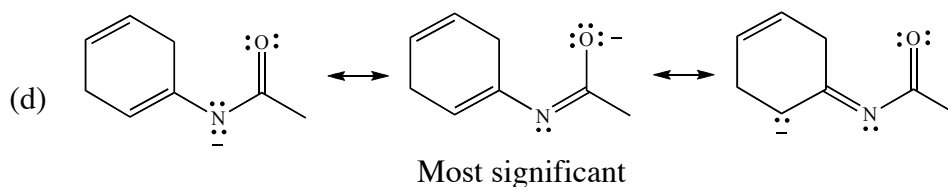
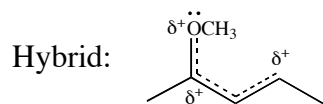
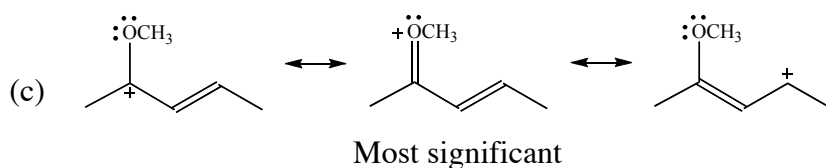
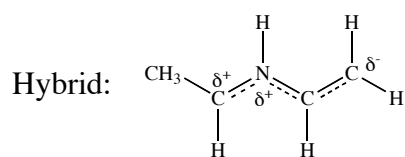
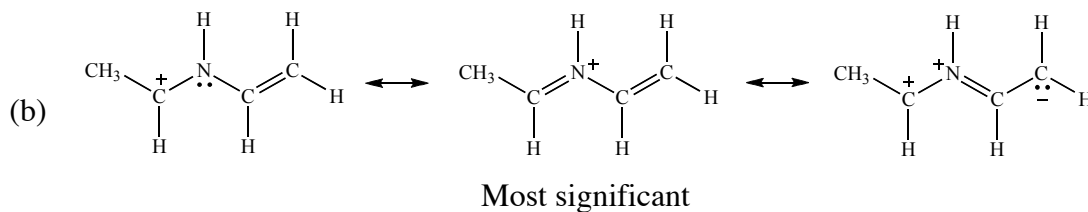
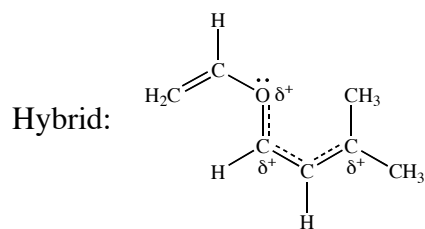


11. Can the electrons of an sp^3 atom ever be involved in resonance?

Practice Problems Solutions

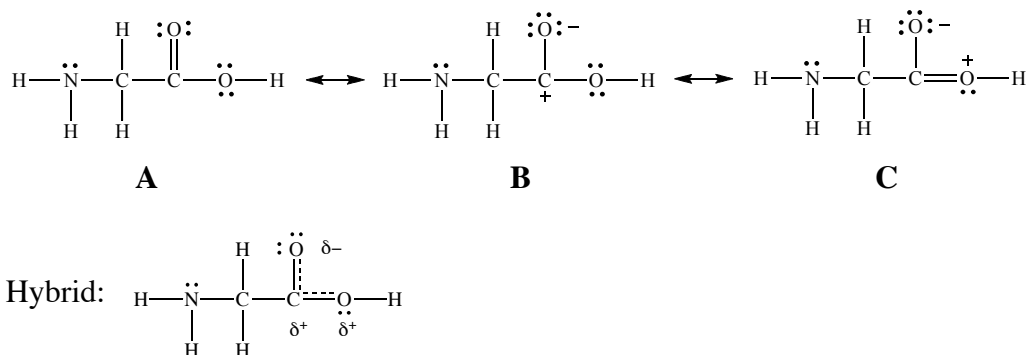


Most significant

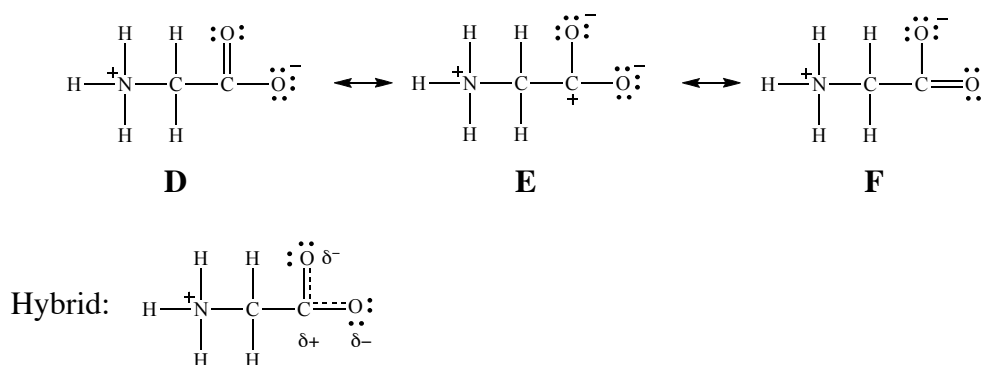


3. Use your judgment. Less significant contributors make lesser contributions to the hybrid. In general, a contributor that violates more than two resonance contributor preference rules is usually not worth considering.

4. (a) Neutral glycine resonance contributors:



Zwitterionic glycine resonance contributors:

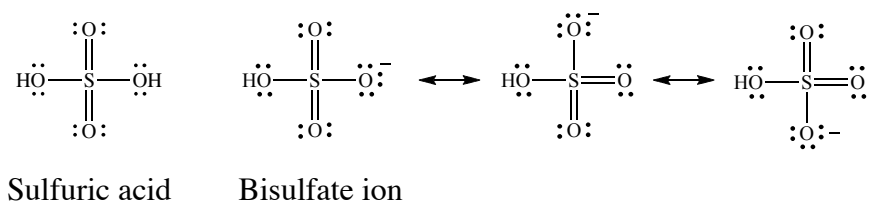


Even though the nitrogen atom in the zwitterionic form bears a positive charge, the charge cannot be delocalized by resonance without giving the nitrogen ten valence electrons.

(b) Neutral glycine: Contributor **A** is most significant. Contributor **B** has an open octet that can be avoided and is therefore of lesser significance. Contributor **C** has formal charges that can be avoided and is also of lesser significance.

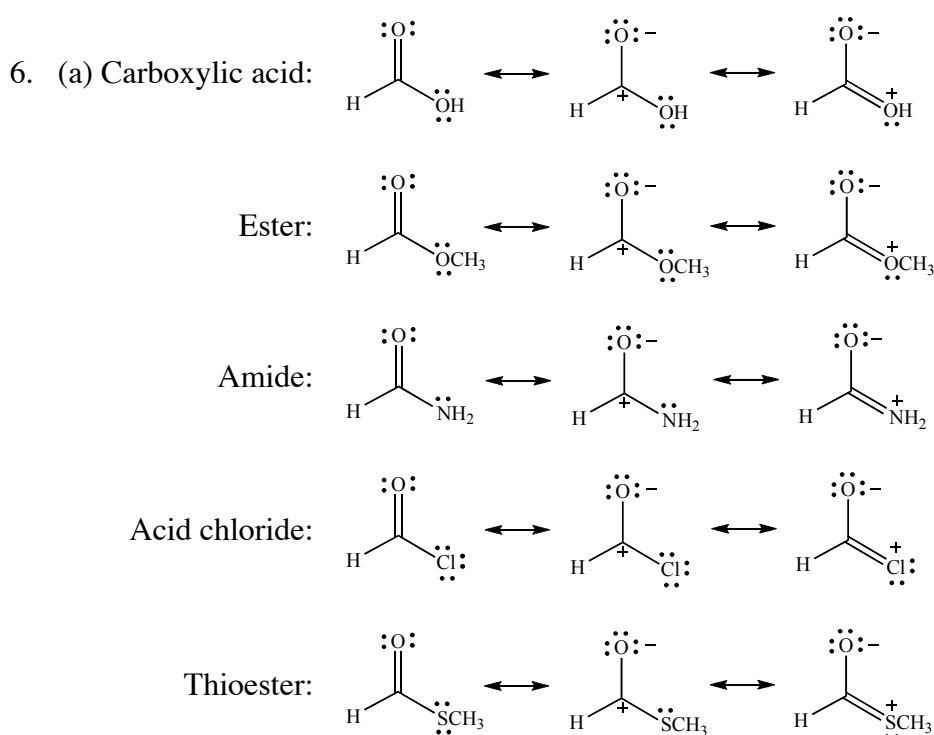
Zwitterionic glycine: Contributor **E** has an avoidable open octet and so is of lesser significance. Contributors **D** and **F** have the same bonding, formal charges, etc., so they are equal in their significance.

5. (a) Sulfuric acid has only one contributor that does not violate any preference rules, whereas bisulfate ion has three.

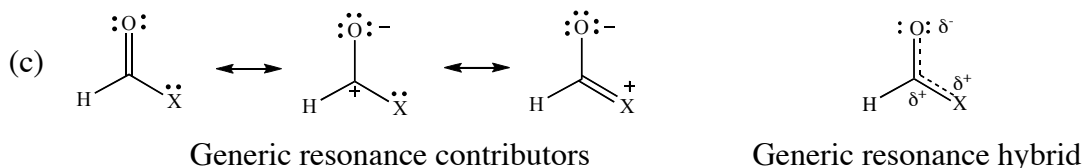


(b) Oxygen is a second-row element and sulfur is a third-row element, so their pi bonding interaction is not as strong (does not provide as much resonance stabilization) as a similar interaction between two second-row elements such as carbon and oxygen. However, sulfuric acid and bisulfate ion both have the same number of sulfur-oxygen bonds, so there is little if any difference in this effect for these two molecules.

(c) Sulfuric acid has just one significant resonance contributor, so it does not have much resonance stabilization. Bisulfate ion has three equally significant resonance contributors, so it enjoys much resonance stabilization. Therefore sulfuric acid readily gives up its hydrogen atom to become bisulfate ion and gain this superb resonance stabilization.

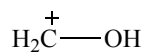


(b) In each case the most important resonance contributor is the first structure shown.

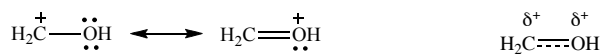


Resonance depends upon atoms, bonds and lone pairs. The functional groups of this question are similar because they all have a carbonyl bearing an atom (X) with at least one lone pair, so their resonance is similar as well.

- (d) The barrier to rotation is due to the partial pi bond between the carbonyl carbon and the X atom. Rotating around this bond destroys resonance because the carbonyl carbon *p* orbital and the X atom lone pair *p* orbital lose their overlap.
- (e) The pi bond interaction is strongest when the atoms involved are in the same row of the periodic table. Since the carbon of the carbonyl is a second-row element, the pi bonds with oxygen and nitrogen are stronger than the pi bonds with chlorine or sulfur. In addition, less electronegative atoms are more willing to share their lone pairs, so a C=N bond is stronger than C=O, and C=S is stronger than C=Cl. Assuming periodic table position carries more weight than electronegativity, and assuming a stronger pi bond gives a higher barrier to rotation, our barrier ranking is: amide (highest) > carboxylic acid or ester (about equal) > thioester > acid chloride.
7. Structure A (below) is not an adequate description of this cation's structure because it has resonance. It is the resonance hybrid, and not any single resonance contributor, that is the best representation of molecular structure.



Structure A

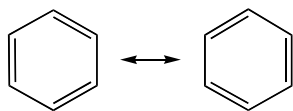


Resonance contributors

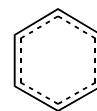
Resonance hybrid

The cation resonance hybrid C–O bond has some pi character, whereas the C–O bond in methanol (CH₃OH) is just a sigma bond. The barrier to rotation for a pi bond (even a partial pi bond) is higher than for the corresponding sigma bond (due to loss of *p* orbital overlap caused by rotation).

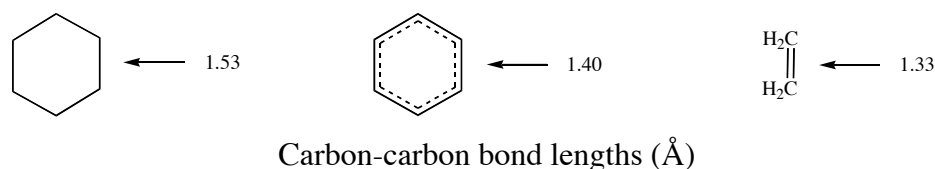
8. (a) When considering any property (such as bond lengths) of a molecule that has resonance we cannot depend on any single resonance contributor but instead we must focus on the resonance hybrid. The resonance hybrid for benzene shows that all six of its carbon-carbon pi bonds are more than single bonds, but not full double bonds, so they are shorter than a typical carbon-carbon sigma bond (as in cyclohexane) but longer than a typical carbon-carbon double bond (as in ethylene).



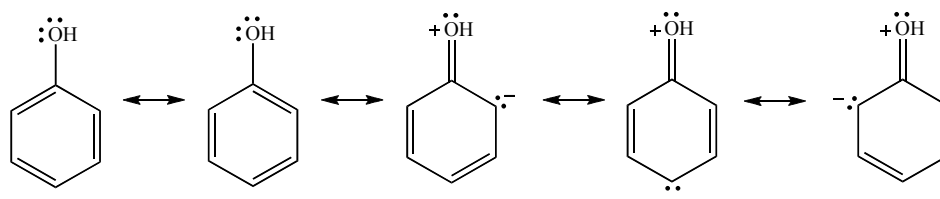
Benzene resonance contributors



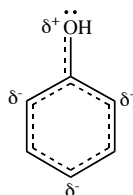
Benzene resonance hybrid



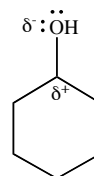
(b) Phenol (C_6H_5OH) has a benzene ring, so any consideration of its properties must start with its resonance hybrid.



Phenol resonance contributors



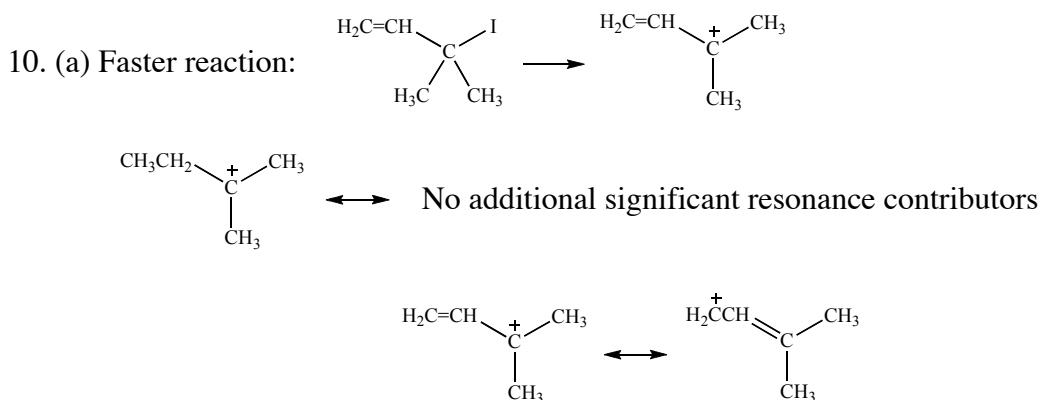
Phenol resonance hybrid



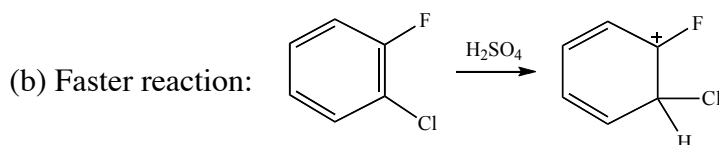
Cyclohexanol

The polarity of the C–O bond of cyclohexanol is controlled only by electronegativity, and has a δ^- on oxygen. In the absence of resonance the C–O bond of phenol would be similar to the C–O bond of cyclohexanol, but resonance withdraws electron density from the oxygen. (This is indicated by the δ^+ on oxygen in the phenol resonance hybrid.) The oxygen of phenol has less electron density than the oxygen of cyclohexanol, and so the C–O bond of phenol is less polar than the C–O bond of cyclohexanol.

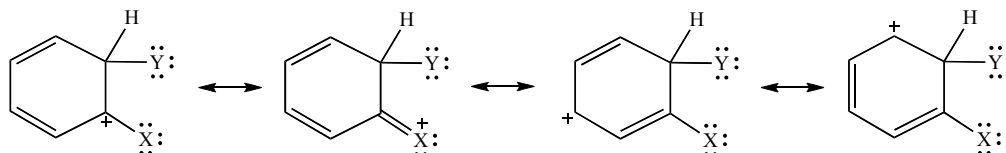
9. Any equilibrium favors the most stable side. If the left is more stable $K_{eq} < 1$. If the right side is more stable $K_{eq} > 1$.
- (a) The formal positive charge of the cation on the left is stabilized by resonance delocalization over the carbons of the benzene ring. In the cation on the right, the formal charge is localized on a single carbon atom. Therefore cation on the left is more stable than the cation on the right, and the equilibrium favors the left side ($K_{eq} < 1$).
- (b) Hydroxide ion and water have no resonance to speak of. Acetic acid (CH_3COOH) has one major and two minor resonance contributors. Acetate ion ($CH_3CO_2^-$) has very significant resonance delocalization due to two important resonance contributors. Everything else being equal, more resonance means more stability, so the right side of the equilibrium is favored ($K_{eq} > 1$).



The product of the second reaction is more stable because it has resonance stabilization of the positive charge whereas the product of the first reaction does not have this stabilization. Using the concept introduced in the question, the more stable product leads to a faster reaction.



The open octet is on carbon (a second row element), so it gains greater resonance stabilization from lone pairs on fluorine (another second row element) than from chlorine (a third row element).



X and Y = Cl or F

You might have argued that chlorine provides better resonance stabilization than fluorine because chlorine has a lower electronegativity (and thus better electron donating power) than fluorine. However, the resonance contributor preference rules remind us that position in the same periodic table row usually outweighs electronegativity.

11. Resonance interaction requires the atoms to have parallel p orbitals. (For two atoms this is a pi bond. For three or more atoms this is conjugation.) An sp^3 atom does not have a p orbital, so its electrons cannot be involved in resonance. The **rare** exception to this rule is when a sigma bond (formed by the overlap of two sp^3 orbitals) is made or broken via resonance.