Organic Chemistry Prep Workshop – Day 3

Lone Pair Electrons

In skeletal structures it is commonplace to leave off the lone pair electrons.

Regardless, you must be able to look at a structure and immediately know if an atom has one or more lone electron pairs.

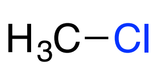
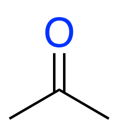
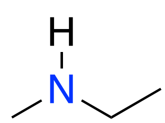
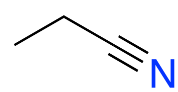
What do you need to know?

The octet rule: atoms desire 8 valence electrons.

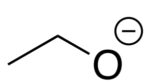
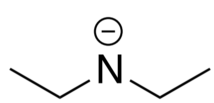
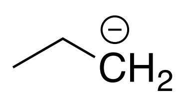
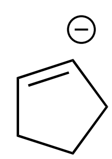
Formal Charge = Valence # − # Bonds − # lone pair electrons *or* # lone pair electrons = Valence # − # Bonds − **Formal Charge**

Determining the number of lone pairs on an atom

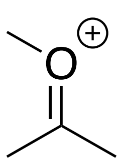
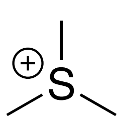
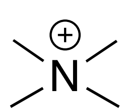
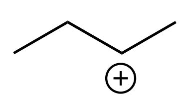
Neutral atoms are easy – Just assume enough lone pair electrons to give the atom an octet.

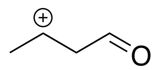
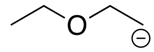
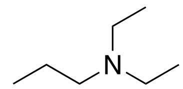
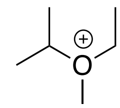
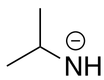
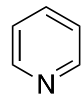
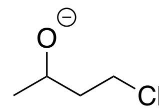
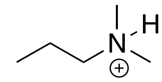





Negatively Charged Atoms – Assume enough lone pair electrons to give the atom an octet.

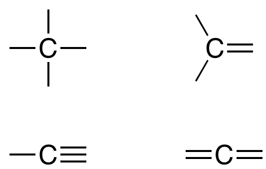
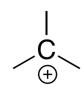
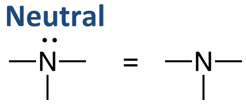
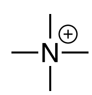
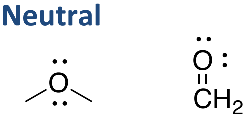
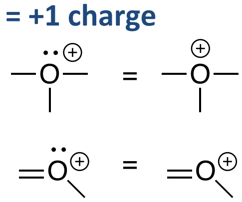
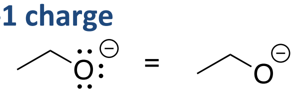





Positively charged carbon – Has only 6 e^- (less than octet).
Other positively charged atoms – Typically have 8 e^- (an octet).

You Try 3-1			
Fill in all lone pairs on each of the molecules shown below.			
			
			

Typical Bonding Patterns

Carbon	**4 bonds, no lone pairs = Neutral** 	**3 bonds, no lone pairs = +1 charge** 	**3 bonds, 1 lone pair = -1 charge**  Commonly drawn without the lone pair. You just need to know it's there.
Nitrogen	**3 bonds, 1 lone pair = Neutral**  Commonly drawn without showing the lone pair.	**4 bonds, no lone pair = +1 charge** 	**2 bonds, 2 lone pairs = -1 charge**  Commonly drawn with just the negative charge. You need to be able to figure out how many lone paris are present.
Oxygen	**2 bonds, 2 lone pairs = Neutral**  You don't have to draw the lone pairs, just be aware they are there.	**3 bonds, 1 lone pair = +1 charge**  Again, its common to not draw in the lone pairs.	**1 bond, 3 lone pairs = -1 charge** 

Curved Arrow Formalism

Curved arrows show electron flow. These arrows are used in reaction mechanisms and in resonance structures to show the movement of electrons.

Every curved arrow has a head and a tail.

Tail Head

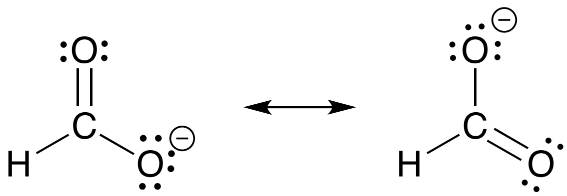
The tail of the arrow should be at a site of high electron density. The head of the arrow points to a site of low electron density (i.e. points to where the electrons are going).

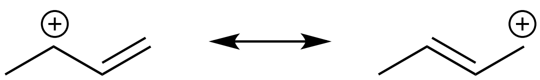
Resonance Structures

Lewis and skeletal structures often fail to accurately represent the true structure of a molecule.

Often lone pair electrons are not truly "localized" on an individual atom. Also, frequently, double bonds are actually somewhere between a double and single bond.

Consider:

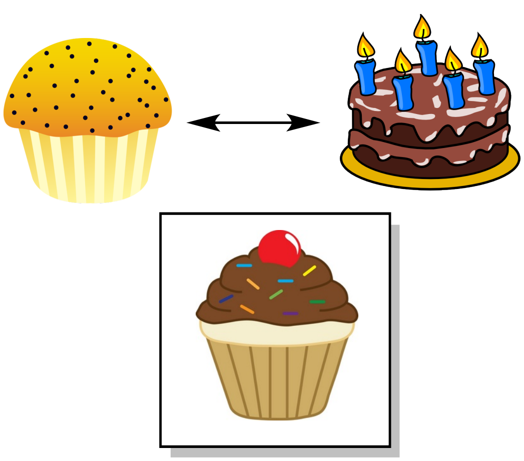


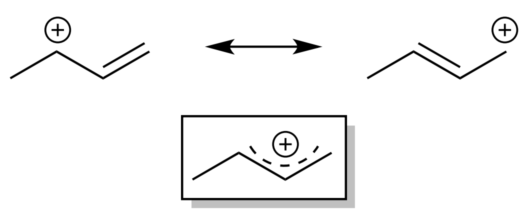


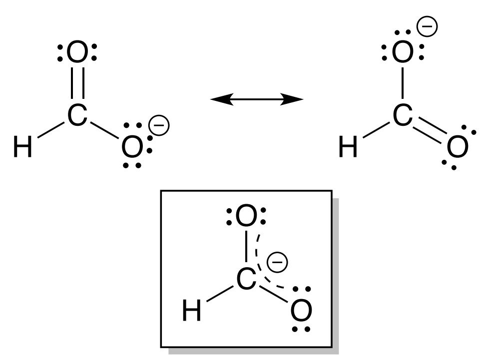
Resonance structures are not in equilibrium or rapidly interconverting. They are simply a means of representing the electron and charge distribution in a molecule.

Resonance Hybrid

Resonance Hybrid – A single entity, the one true structure of a molecule.



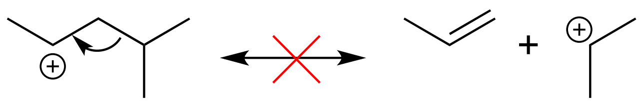




Rules for Drawing Resonance Structures

- Do not break or move a single bond.
- Atom connectivity must not be changed.
- Never exceed an octet for 2nd row elements.
- It's okay to have less than an octet on 2nd row elements.
- Only electrons in p-bonds and non-bonding electrons can be moved.

Examples of Resonance Violations



Rules Violated:
- Do not break or move a single bond.
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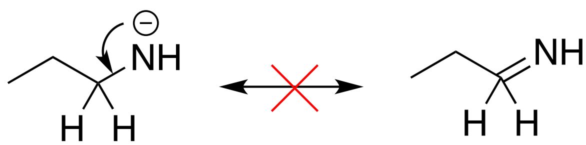
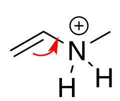
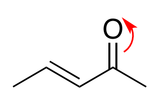
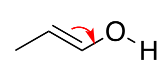
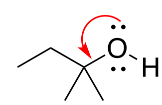
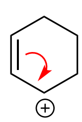
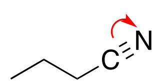
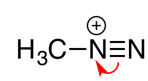
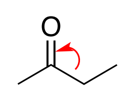


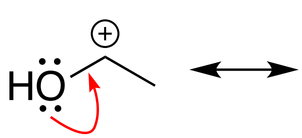
Rules Violated:
- Never exceed an octet for 2nd row elements.

You Try 3-2			
For each structure below, determine whether or not the electron movement shown violates any rules of resonance.			
			
			

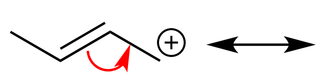
Curved Arrows and Resonance

When an arrowhead points to a bond, you are forming a new bond at that location.

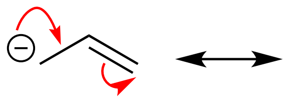
Tail at a lone pair:

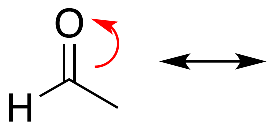


Tail at a bond:



When an arrowhead points to an atom, you are putting a new lone pair of electrons on that atom.





Tracking Charges in Resonance Structures

The formal charge calculation can always be used.

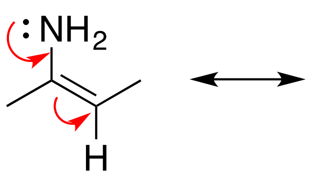
Be sure to maintain charge balance!

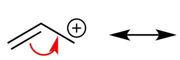
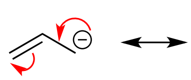
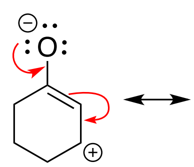
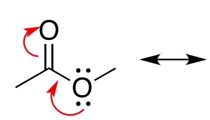
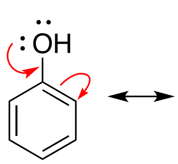
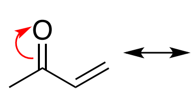
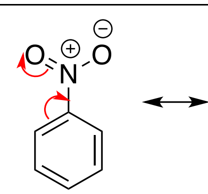
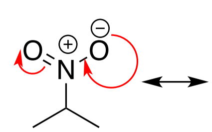
If an atom shares its electron pair, its charge increases by +1.

0 → +1 -1 → 0

If an atom accepts an electron pair, its charge decreases by +1.

0 → -1 +1 → 0

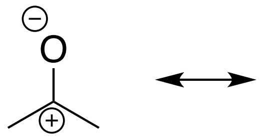


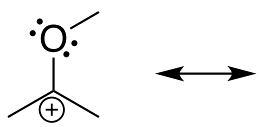
You Try 3-3			
For each structure below, draw the other resonance structure with appropriate formal charges.			
			
			

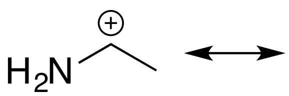
Resonance Patterns

Two Atom Systems:

1. Lone Pair Next to a Positive Charge



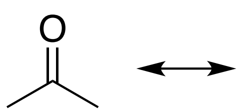


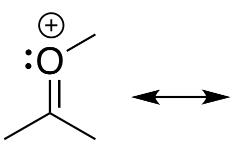


Requires only <u>one</u> arrow.

The atom with the lone pair may be neutral or negatively charged.

2. π-bond between two atoms with different electronegativities.



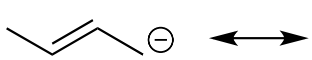


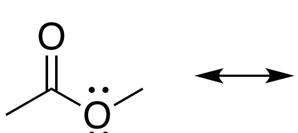
Requires only <u>one</u> arrow.

This pattern is just the reverse of pattern 1.

Three Atom Systems:

3. A lone pair next to a π-bond.



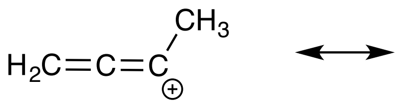


Requires <u>two</u> curved arrows.

The atom with the lone pair may be negatively charged or neutral.

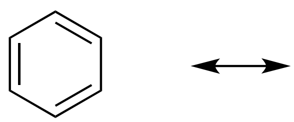
4. A positive charge next to a π-bond.

Requires only <u>one</u> arrow.



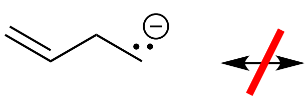
Cyclic Systems:

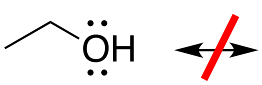
5. A cyclic array of alternating π-bonds.



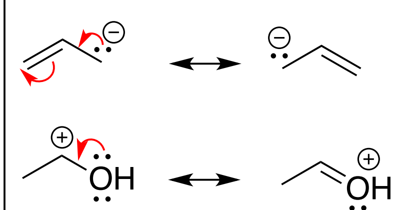
Mistakes to Avoid

Don't move a lone pair if it is not next to a π-bond or a positive charge.

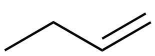




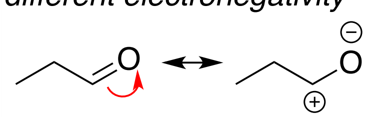
Valid Movements



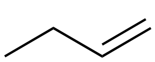
Generally should not move a π-bond between two carbon atoms to get adjacent charges.



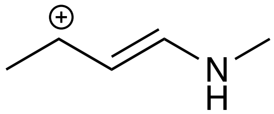
Valid Movement
π-bond between atoms of different electronegativity

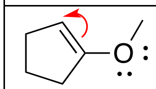
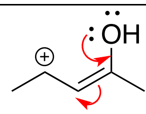
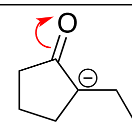
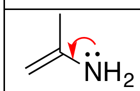
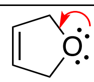
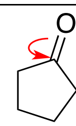


Don't move a π-bond to an atom that results in exceeding the atoms octet.



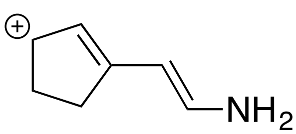
Don’t move electrons that result in three or more charges on a structure.

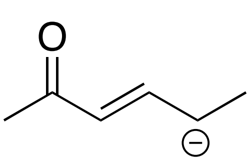


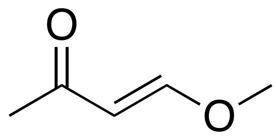
You Try 3-4		
Explain why each electron movement shown does not give a valid resonance structure. Then, provide an alternative if possible.		
		
		

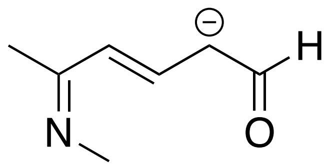
Molecules with Multiple Resonance Structures

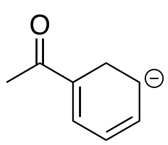
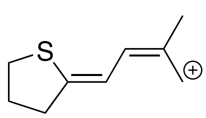
- Generally start at the charge if one is present.
- If uncharged, start at a lone pair of electrons.
- Focus on two or three atoms at a time.
- Ensure charge balance.









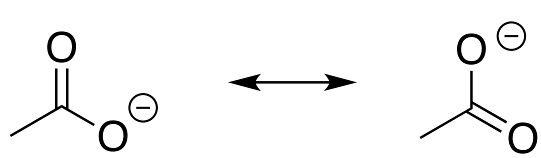
You Try 3-5
Draw all of the valid resonance structures for each molecule below.



Are all Resonance Structures Equivalent?

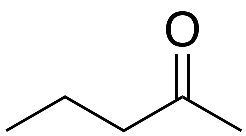
NO. Remember that individual resonance structures are not true structures. The true structure of a molecule is a resonance hybrid. The individual resonance structures that make up a hybrid are not always equivalent. In many cases, the resonance hybrid looks much more like one resonance structure than another.

Relative Importance of Resonance Structures

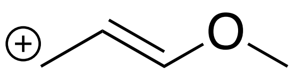
1. Equivalent structures have equal importance.



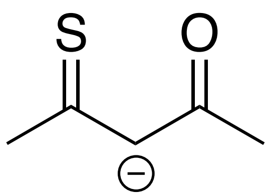
2. A structure that minimizes charges is more important.



3. A structure where all atoms have an octet is more important.



4. A structure that puts a negative charge on a more electronegative is more important.



You Try 3-6

For each set of resonance structures, circle the structure that is the major contributor to the resonance hybrid.