

Resonance Tutorial – Chemistry 233

Lone Pair Madness: How do I know when and where to put lone pair electrons?

In skeletal structures, it is common for lone pair electrons to be left off. You will often need to use your knowledge of formal charges to determine how many, if any, lone pairs are present. Neutral compounds are easy – just assume enough lone pair electrons to give you an octet.

E.g. If you have a compound that has oxygen with 3 bonds and a positive charge:

Formal Charge = Valence # - # bonds - # non-bonding electrons

Oxygen has a valence of 6

Set up an equation: $+1 = 6 - 3 - ?$ Solve for “?” $\rightarrow ? = 2$

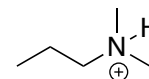
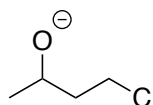
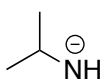
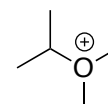
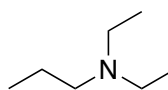
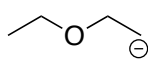
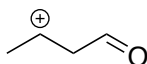
Oxygen has 2 non-bonding e- (**1 lone pair**)



The table below will help guide you:


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 pairs 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

Practice: Fill in all lone pair electrons on each of the molecules below.



Curved Arrows and Resonance

Curved arrows show electron flow; they are used in reaction mechanisms and to show electron movement in resonance structures.

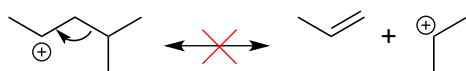
Every curved arrow has a head and a tail. tail  head

The direction a curved arrow is drawn is **very** important. The tail of the arrow should be at a site of electron density (lone pair, bond). The head of the arrow shows where those electrons are going.

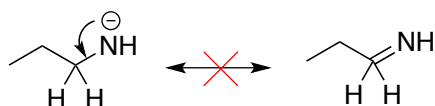
Rules for Resonance Structures:

- Do not break single bonds.
- Atoms connectivity must not be changed.
- Never exceed an octet for 2nd row elements.
- It's okay to have less than an octet of electrons on second row elements.
- Only electrons from π -bonds and non-bonding electrons (lone pair, radical) can be moved.

Examples of Resonance Violations:



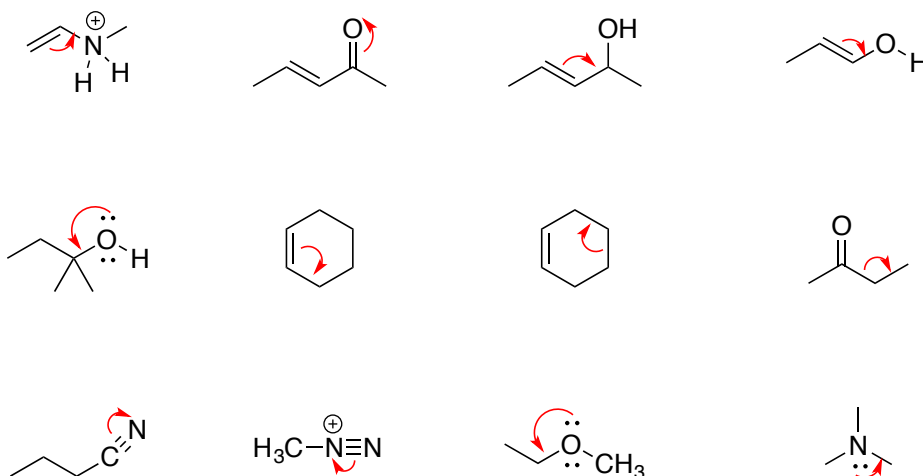
Not resonance structures!
Can't break the single bond, because that changes the atom connectivity.



Not resonance structures!
This violates the octet rule. Here you are exceeding the octet of the carbon (it has 5 bonds).

In skeletal structures, it is common for lone pair electrons to be left off. You will often need to use your knowledge of formal charges to determine how many, if any, lone pairs are present. Neutral compounds are easy – just assume enough lone pair electrons to give you an octet.

Practice: For each of the structures below indicate whether or not the curved arrow violates any rules of resonance.

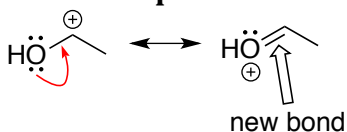


Curved Arrow Formalism

The exact placement of the arrow head and tail is very important. The table below shows a few general arrow pushing patterns.

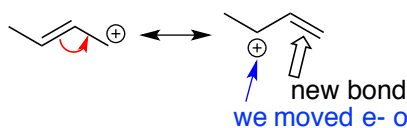
When an arrow head points to a bond you are forming a new bond at that location.

Tail at a lone pair:



- Oxygen is now sharing one of its lone pairs in the form of a bond.
- We took electrons away from O, so it gets the + charge.
- We put electrons into the neighboring C (in the form of a bond), so it loses the + charge

Tail at a bond:



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

lone pair is being pushed into a bond

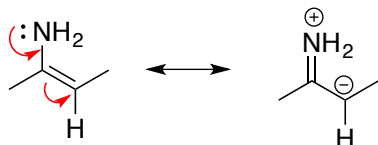


the electrons in the double bond are being pushed onto the C in the form of a lone pair.

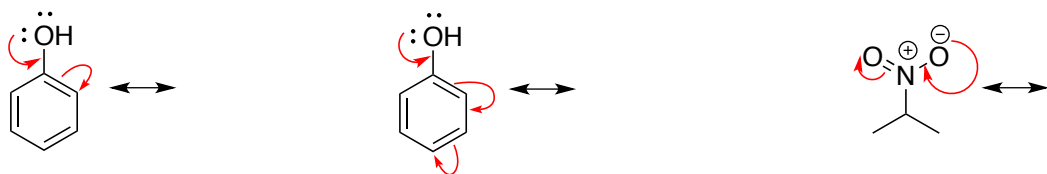
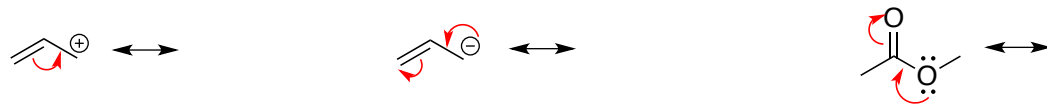
Formal Charges in Resonance Structures

Resonance structures will often contain formal charges. It is very important to assign them properly.

In the example below, nitrogen has a lone pair. We can move these lone pair electrons to form a nitrogen-carbon double bond. In doing so, this would appear to give carbon more than an octet of electrons, however since the carbon contains a π -bond, those π -electrons can be pushed over to the neighboring carbon. The result of this process gives us a nitrogen with 4-bonds (+1 charge), and a carbon with 3-bonds and a lone pair (-1 charge).



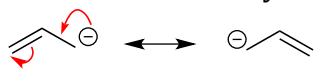
Practice: For each of the structures below, draw the resonance structure with appropriate formal charges.



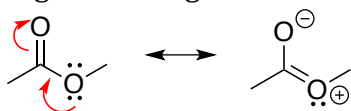
Major Patterns for Resonance Structures

1. Lone Pair Next to a π -bond (allylic lone pair)

- This system requires two curved arrows to show the resonance structure.
- If the atom with the lone pair bears a negative charge, it transfers the negative charge to the atom that ultimately receives the lone pair.

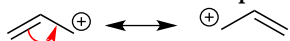


- If the atom with the lone pair does not have a negative charge, then it will obtain a positive charge in its resonance structure, while the atom that receives the lone pair will obtain a negative charge



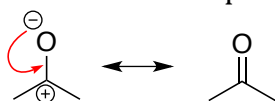
2. Positive Charge Next to a π -bond (allylic cation)

- This system requires only one curved arrow.
- The atom with the positive charge gets a new π -bond, while the atom that previously had the π -bond obtains the positive charge.

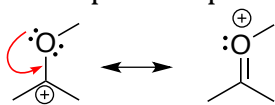


3. A Lone Pair Next to a Positive Charge

- This system requires only one curved arrow.
- The atom next to the positive charge may have a negative charge. In this case the resonance structure ends up neutral.

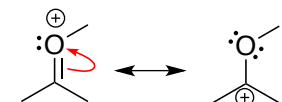
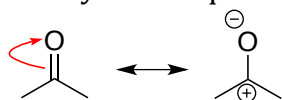


- The atom next to the positive charge may be neutral. In this case the atom with the lone pair ends up with a positive charge in the resonance structure.

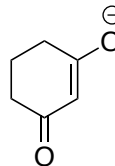
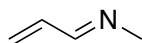
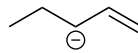
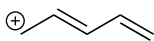
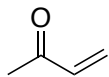


4. A π -Bond Between Two Atoms With Different Electronegativities

- This is basically the reverse of pattern 3.
- This system requires only one curved arrow.



Practice: Draw resonance structures for each of the following. In some cases you will be able to draw multiple resonance structures.

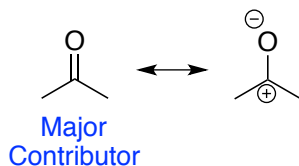


Are all Resonance Structures Equivalent?

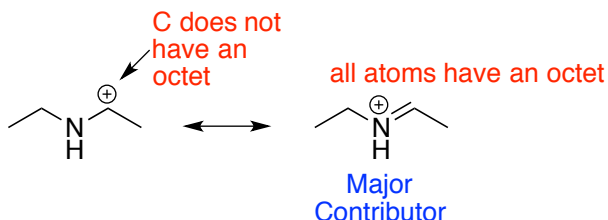
NO. Remember that individual resonance structures are not true structures. The true structure of a molecule is a resonance hybrid. The individual resonance structures that make up a hybrid are not always equivalent. In many cases, the resonance hybrid looks much more like one resonance structure than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

General Rules:

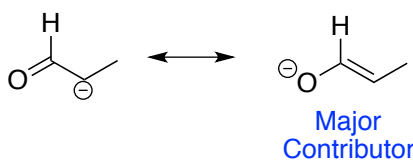
1. Resonance structures that minimize charges are more major contributors to the hybrid.



2. Resonance structures where all atoms have an octet are more major contributors.



3. Resonance structures that put the negative charge on a more electronegative atom are more major contributors to the resonance hybrid.



Practice: Draw all of the resonance structures for the compound shown below. Circle the resonance structure that is the major contributor to the resonance hybrid.

