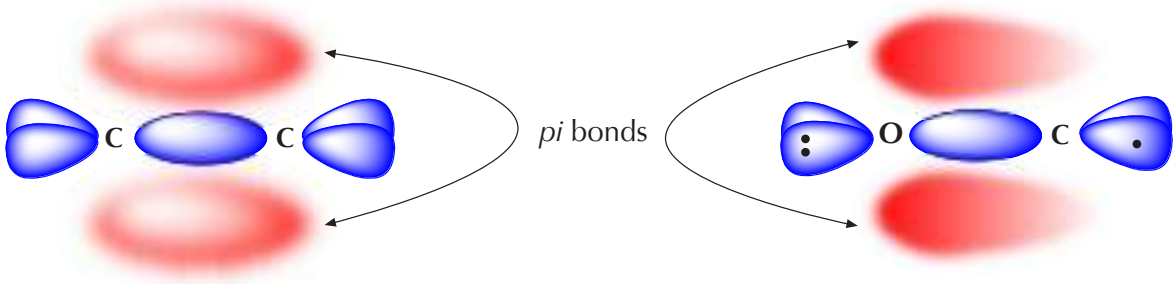
ELECTRON DELOCALIZATION AND RESONANCE

LEARNING OBJECTIVES

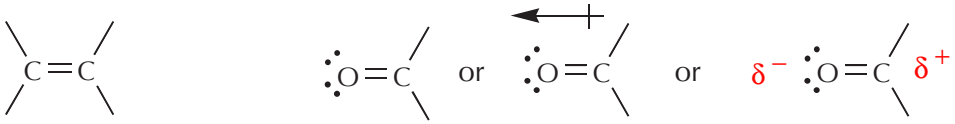
To introduce the concept of electron delocalization from the perspective of molecular orbitals, to understand the relationship between electron delocalization and resonance, and to learn the principles of electron movement used in writing resonance structures in Lewis notation, known as the *curved arrow formalism*.

MOBILITY OF *Pi* ELECTRONS AND UNSHARED ELECTRON PAIRS

Now that we understand the difference between sigma and *pi* electrons, we remember that the *pi* bond is made up of loosely held electrons that form a diffuse cloud which can be easily distorted. This can be illustrated by comparing two types of double bonds, one polar and one nonpolar. The C=C double bond on the left below is nonpolar. Therefore the *pi* electrons occupy a relatively symmetric molecular orbital that's evenly distributed (shared) over the two carbon atoms. The C=O double bond, on the other hand, is polar due to the higher electronegativity of oxygen. The *pi* cloud is distorted in a way that results in higher electron density around oxygen compared to carbon. Both atoms still share electrons, but the electrons spend more time around oxygen. The drawing on the right tries to illustrate that concept.



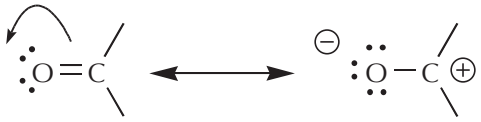
Using simple Lewis formulas, or even line-angle formulas, we can also draw some representations of the two cases above, as follows.



nonpolar *pi* bond

polar *pi* bond representations

The dynamic nature of *pi* electrons can be further illustrated with the use of arrows, as indicated below for the polar C=O bond:



The **CURVED ARROW FORMALISM** is a convention used to represent the movement of electrons in molecules and reactions according to certain rules. We'll study those rules in some detail. For now, we keep a few things in mind:

a) Curved arrows always represent the movement of electrons, not atoms.

b) Electrons always move towards more electronegative atoms or towards positive charges.

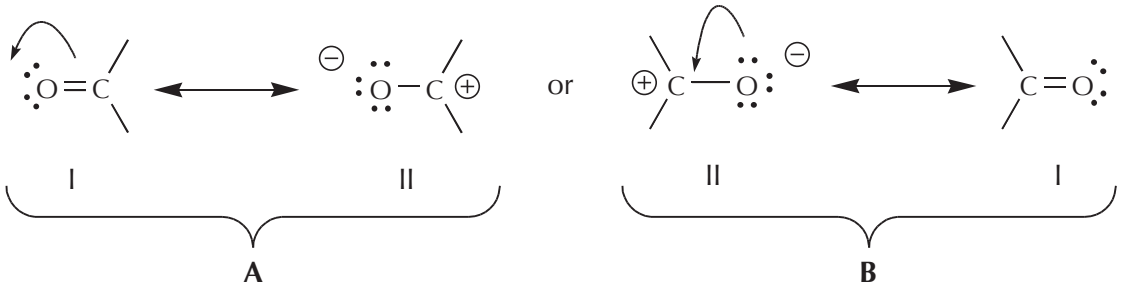
We notice that the two structures shown above as a result of "***pushing electrons***" towards the oxygen are **RESONANCE STRUCTURES**. That is to say, they are both valid Lewis representations of the same species. The actual species is therefore a hybrid of the two structures. We conclude that:

Curved arrows can be used to arrive from one resonance structure to another by following certain rules.

Just like *pi* electrons have a certain degree of mobility due to the diffuse nature of *pi* molecular orbitals, **unshared electron pairs can also be moved with relative ease because they are not engaged in bonding**. No bonds have to be broken to move those electrons. As a result, we keep in mind the following principle:

Curved arrows usually originate with pi electrons or unshared electron pairs, and point towards more electronegative atoms, or towards partial or full positive charges.

Going back to the two resonance structures shown before, we can use the curved arrow formalism either to arrive from structure I to structure II, or vice versa.



In case **A**, the arrow originates with *pi* electrons, which move towards the more electronegative oxygen. In case **B**, the arrow originates with one of the unshared electron pairs, which moves towards the positive charge on carbon. We further notice that *pi* electrons from one structure can become unshared electrons in another, and vice versa. We'll look at additional guidelines for how to use mobile electrons later.

Finally, in addition to the above, we notice that the oxygen atom, for example, is sp^2 hybridized (trigonal planar) in structure I, but sp^3 hybridized (tetrahedral) in structure II. So, which one is it? Again, what we are talking about is the real species. The real species is a hybrid that contains contributions from both resonance structures. In this particular case, the best we can do for now is issue a qualitative statement: since structure I is the major contributor to the hybrid, we can say that the oxygen atom in the actual species is mostly trigonal planar because it has greater sp^2 character, but it still has some tetrahedral character due to the minor contribution from structure II. We'll explore and expand on this concept in a variety of contexts throughout the course.

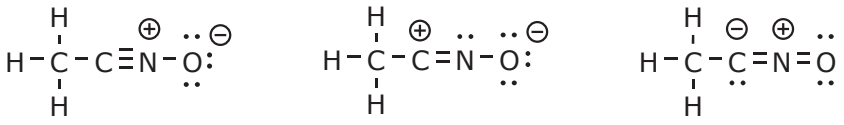
What about sigma electrons, that is to say those forming part of single bonds? These bonds represent the "glue" that holds the atoms together and are a lot more difficult to disrupt. As a result, they are not as mobile as *pi* electrons or unshared electrons, and are therefore rarely moved. There are however some exceptions, notably with highly polar bonds, such as in the case of HCl illustrated below. We will not encounter such situations very frequently.



This representation better conveys the idea that the H–Cl bond is highly polar.

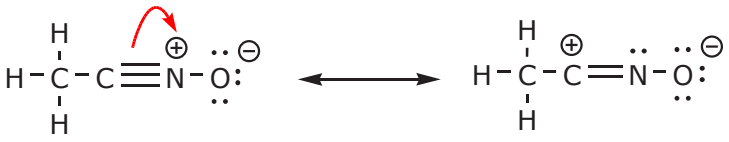
USING CURVED ARROWS - ADDITIONAL CONCEPTS

We now go back to an old friend of ours, CH_3CNO, which we introduced when we first talked about resonance structures. We use this compound to further illustrate how mobile electrons are "pushed" to arrive from one resonance structure to another.



I II III

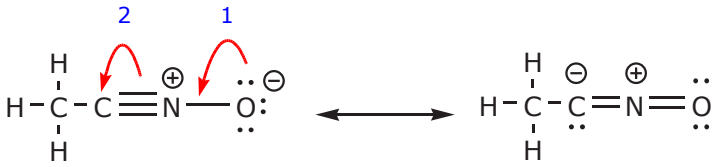
The movement of electrons that takes place to arrive at structure II from structure I starts with the triple bond between carbon and nitrogen. We'll move one of the two *pi* bonds that form part of the triple bond towards the positive charge on nitrogen, as shown:



I II

When we do this, we pay close attention to the new status of the affected atoms and make any necessary adjustments to the charges, bonds, and unshared electrons to preserve the validity of the resulting formulas. In this case, for example, the carbon that forms part of the triple bond in structure I has to acquire a positive charge in structure II because it's lost one electron. The nitrogen, on the other hand, is now neutral because it gained one electron and it's forming three bonds instead of four.

We can also arrive from structure I to structure III by pushing electrons in the following manner. The arrows have been numbered in this example to indicate which movement starts first, but that's not part of the conventions used in the curved arrow formalism.



I III

As we move a pair of unshared electrons from oxygen towards the nitrogen atom as shown in step 1, we are forced to displace electrons from nitrogen towards carbon as shown in step 2. Otherwise we would end up with a nitrogen with 5 bonds, which is impossible, even if only momentarily. Again, notice that in step 1 the arrow originates with an unshared electron pair from oxygen and moves towards the positive charge on nitrogen. A new *pi* bond forms between nitrogen and oxygen. At the same time, the *pi* electrons being displaced towards carbon in step 2 become a pair of unshared electrons in structure III. Finally, the hybridization state of some atoms also changes. For example the carbon atom in structure I is *sp* hybridized, but in structure III it is sp^3 hybridized.

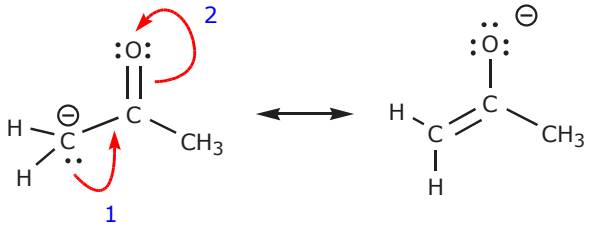
You may want to play around some more and see if you can arrive from structure II to structure III, etc. However, be warned that sometimes it is trickier than it may seem at first sight.

Here are some additional rules for moving electrons to write resonance structures:

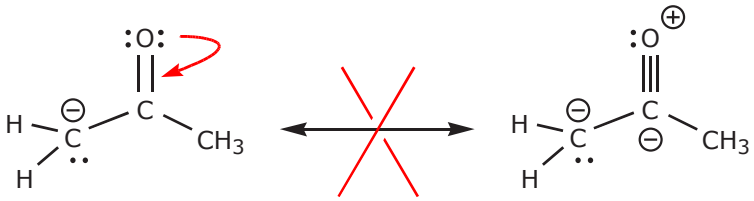
1. Electron pairs can only move to adjacent positions. Adjacent positions means neighboring atoms and/or bonds.

2. The Lewis structures that result from moving electrons must be valid and must contain the same net charge as all the other resonance structures.

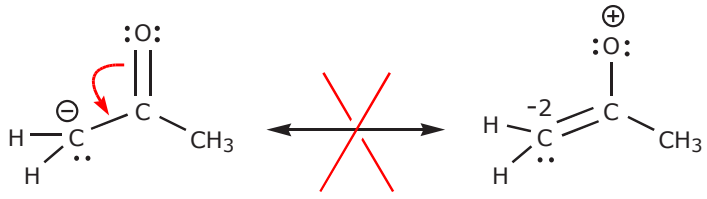
The following example illustrates how a lone pair of electrons from carbon can be moved to make a new *pi* bond to an adjacent carbon, and how the *pi* electrons between carbon and oxygen can be moved to become a pair of unshared electrons on oxygen. None of the previous rules has been violated in any of these examples.



Now let's look at some examples of HOW NOT TO MOVE ELECTRONS. Using the same example, but moving electrons in a different way, illustrates how such movement would result in invalid Lewis formulas, and therefore is unacceptable. Not only are we moving electrons in the wrong direction (away from a more electronegative atom), but the resulting structure violates several conventions. First, the central carbon has five bonds and therefore violates the octet rule. Second, the overall charge of the second structure is different from the first. To avoid having a carbon with five bonds we would have to destroy one of the C–C single bonds, destroying the molecular skeleton in the process.

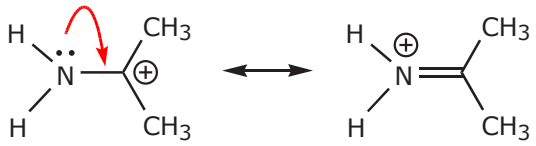


In the example below electrons are being moved towards an area of high electron density (a negative charge), rather than towards a positive charge. In addition, the octet rule is violated for carbon in the resulting structure, where it shares more than eight electrons.

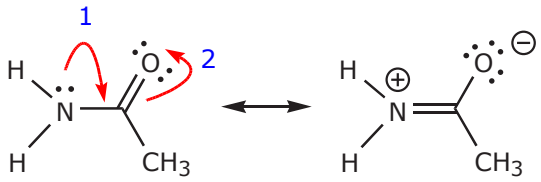


Additional examples further illustrate the rules we've been talking about.

(a) Unshared electron pairs (lone pairs) located on a given atom can only move to an adjacent position to **make a new *pi* bond** to the next atom.

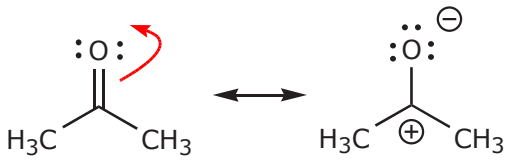


(b) Unless there is a positive charge on the next atom (carbon above), other electrons will have to be displaced to preserve the octet rule. In resonance structures these are almost always *pi* electrons, and almost never sigma electrons.

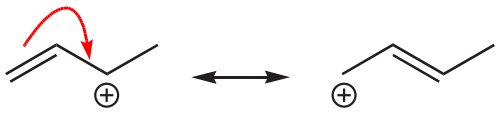


As the electrons from the nitrogen lone pair move towards the neighboring carbon to make a new *pi* bond, the *pi* electrons making up the C=O bond must be displaced towards the oxygen to avoid ending up with five bonds to the central carbon.

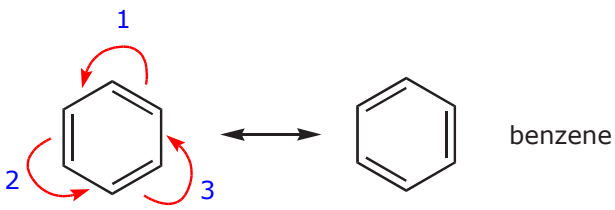
(c) As can be seen above, ***pi* electrons** can move towards one of the two atoms they share **to form a new lone pair**. In the example above, the *pi* electrons from the C=O bond moved towards the oxygen to form a new lone pair. Another example is:t



(d) *pi* electrons can also move to an adjacent position **to make new *pi* bond**. Once again, the octet rule must be observed:

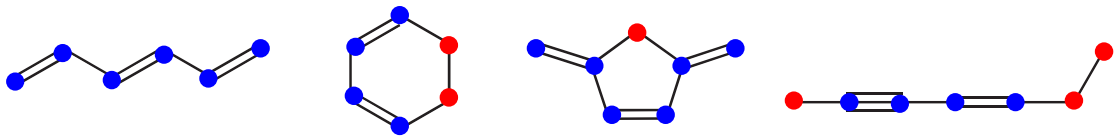


One of the most common examples of this feature is observed when writing resonance forms for benzene and similar rings.



DELOCALIZATION, CONJUGATED SYSTEMS, AND RESONANCE ENERGY

The presence of alternating *pi* and sigma bonds in a molecule such as benzene is known as a **conjugated system,** or **conjugated *pi* bonds**. Conjugated systems can extend across the entire molecule, as in benzene, or they can comprise only part of a molecule. A conjugated system always starts and ends with a *pi* bond (i.e. an sp^2 or an *sp*-hybridized atom), or sometimes with a charge. The atoms that form part of a conjugated system in the examples below are shown in blue, and the ones that do not are shown in red. Most of the times it is sp^3 hybridized atoms that break a conjugated system.

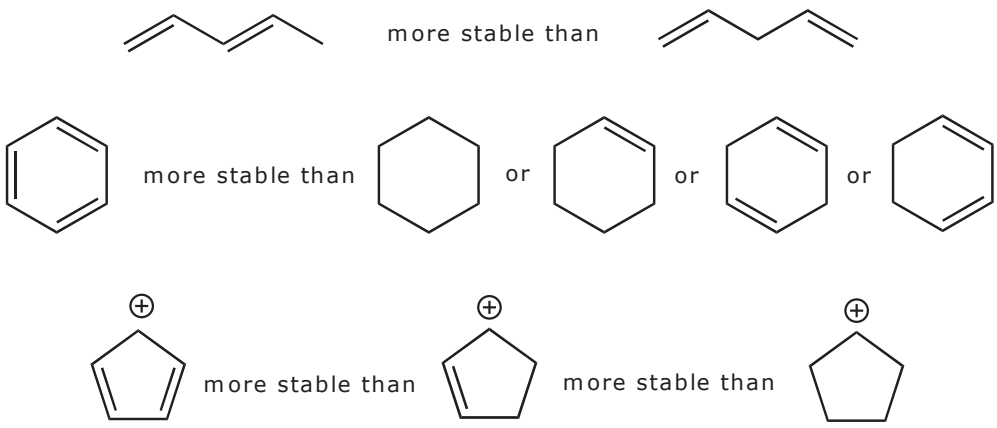


Practically every time there are *pi* bonds in a molecule, especially if they form part of a conjugated system, there is a possibility for having resonance structures, that is, several valid Lewis formulas for the same compound. What resonance forms show is that there is **electron delocalization**, and sometimes **charge delocalization**. All the examples we have seen so far show that electrons move around and are not static, that is, they are delocalized. **Charge delocalization is a stabilizing force** because it spreads energy over a larger area rather than keeping it confined to a small area. Since electrons are charges, the presence of delocalized electrons brings extra stability to a system compared to a similar system where electrons are localized. The stabilizing effect of charge and electron delocalization is known as **resonance energy**.

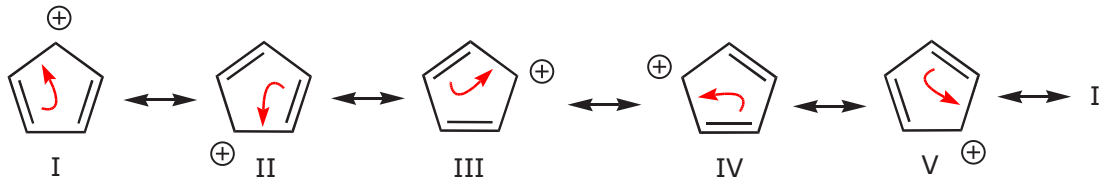
Since conjugation brings up electron delocalization, it follows that **the more extensive the conjugated system, the more stable the molecule** (i.e. the lower its potential energy). If there are positive or negative charges, they also spread out as a result of resonance.The corollary is that

the more resonance forms one can write for a given system, the more stable it is .
That is, the greater its resonance energy .

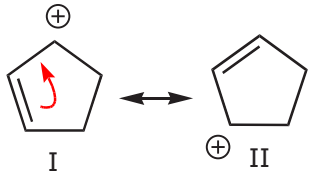
Examine the following examples and write as many resonance structures as you can for each to further explore these points:



Let's look for a moment at the three structures in the last row above. In the first structure, delocalization of the positive charge and the *pi* bonds occurs over the entire ring. This becomes apparent when we look at all the possible resonance structures as shown below.



In the second structure, delocalization is only possible over three carbon atoms. This is demonstrated by writing all the possible resonance forms below, which now number only two.

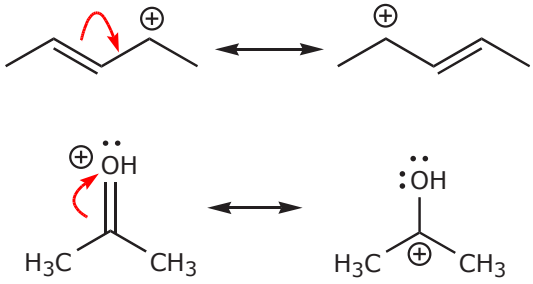


Finally, the third structure has no delocalization of charge or electrons because no resonance forms are possible. Therefore, it is the least stable of the three. This brings us to the last topic. How do we recognize when delocalization is possible? Let's look at some delocalization setups, that is to say, structural features that result in delocalization of electrons.

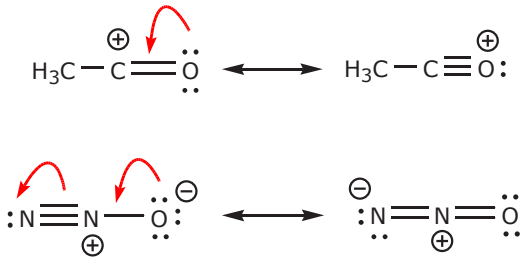
DELOCALIZATION SETUPS

There are specific structural features that bring up electron or charge delocalization. **The presence of a conjugated system is one of them**. Other common arrangements are:

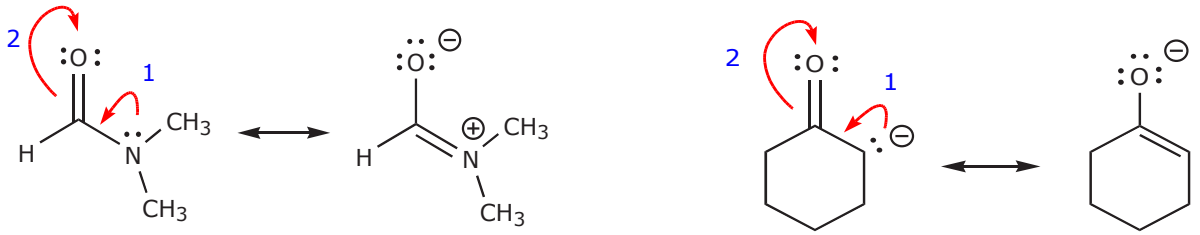
(a) The presence of a positive charge next to a *pi* bond. The positive charge can be on one of the atoms that make up the *pi* bond, or on an adjacent atom.



(b) The presence of a positive charge next to an atom bearing lone pairs of electrons.

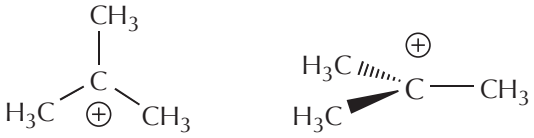


(c) The presence of a *pi* bond next to an atom bearing lone pairs of electrons.

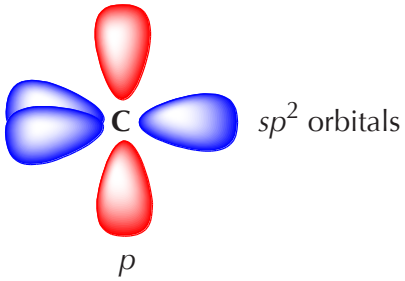


ORBITAL PICTURE OF DELOCALIZATION

The orbital view of delocalization can get somewhat complicated. For now we're going to keep it at a basic level. We start by noting that sp^2 carbons actually come in several varieties. Two of the most important and common are neutral sp^2 carbons and positively charged sp^2 carbons. Substances containing neutral sp^2 carbons are regular alkenes. Species containing positively charged sp^2 carbons are called **carbocations**. The central carbon in a carbocation has trigonal planar geometry, and the unhybridized *p* orbital is empty. The following representations convey these concepts.

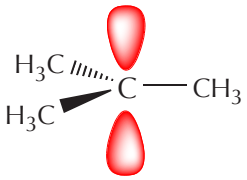


Top and side view of a carbocation in Lewis and 3-D notation



Orbital view of a carbocation. The unhybridized *p* orbital is empty

A combination of orbital and Lewis or 3-D formulas is a popular means of representing certain features that we may want to highlight. For example, if we're not interested in the sp^2 orbitals and we just want to focus on what the *p* orbitals are doing we can use the following notation.



Let's now focus on two simple systems where we know delocalization of *pi* electrons exists. One is a system containing two *pi* bonds in conjugation, and the other has a *pi* bond next to a positively charged carbon. We can represent these systems as follows.

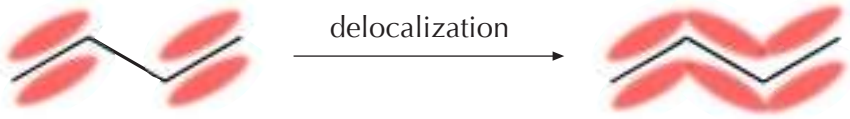


Line angle and orbital picture of a simple conjugated system

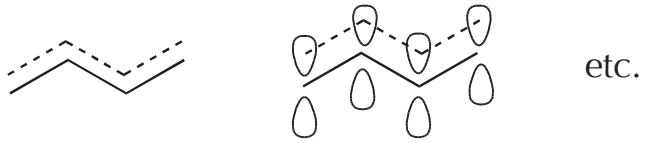


Line angle and orbital picture of a system containing a carbocation next to a *pi* bond

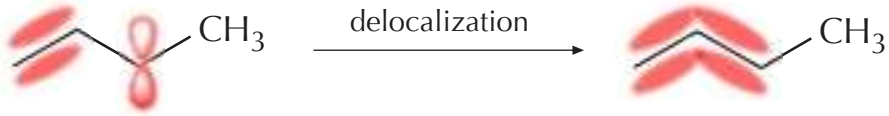
If we focus on the orbital pictures, we can immediately see the potential for electron delocalization. The two *pi* molecular orbitals shown in red on the left below are close enough to overlap. Overlapping is a good thing because it delocalizes the electrons and spreads them over a larger area, bringing added stability to the system.



It is however time-consuming to draw orbitals all the time. The following representations are used to represent the delocalized system.



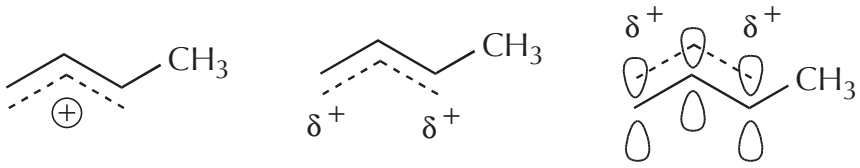
A similar process applied to the carbocation leads to a similar picture.



The resonance representation conveys the idea of delocalization of charge and electrons rather well.



Finally, the following representations are sometimes used, but again, the simpler they are, the less accurately they represent the delocalization picture.



There will be plenty of opportunity to observe more complex situations as the course progresses.