CHAPTER 2

RESONANCE

In this chapter, you will learn the tools that you need to draw resonance structures with proficiency. I cannot adequately stress the importance of this skill. Resonance is the one topic that permeates the entire subject matter from start to finish. It finds its way into every chapter, into every reaction, and into your nightmares if you do not master the rules of resonance. You cannot get an A in this class without mastering resonance. So what is resonance? And why do we need it?

2.1 WHAT IS RESONANCE?

In Chapter 1, we introduced one of the best ways of drawing molecules, bond-line structures. They are fast to draw and easy to read, but they have one major deficiency: they do not describe molecules perfectly. In fact, no drawing method can completely describe a molecule using only a single drawing. Here is the problem.

Although our drawings are very good at showing which atoms are connected to each other, our drawings are not good at showing where all of the electrons are, because electrons aren't really solid particles that can be in one place at one time. All of our drawing methods treat electrons as particles that can be placed in specific locations. Instead, it is best to think of electrons as *clouds of electron density*. We don't mean that electrons fly around in clouds; we mean that electrons *are* clouds. These clouds often spread themselves across large regions of a molecule.

So how do we represent molecules if we can't draw where the electrons are? The answer is resonance. We use the term *resonance* to describe our solution to the problem: we use more than one drawing to represent a single molecule. We draw several drawings, and we call these drawings *resonance structures*. We meld these drawings into one image in our minds. To better understand how this works, consider the following analogy.

Your friend asks you to describe what a nectarine looks like, because he has never seen one. You aren't a very good artist so you say the following:

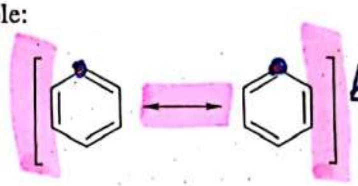
> *Picture a peach in your mind, and now picture a plum in your mind. Well, a nectarine has features of both: the inside tastes like a peach, but the outside is smooth like a plum. So take your image of a peach together with your image of a plum and meld them together in your mind into one image. That's a nectarine.*

It is important to realize that a nectarine does not switch back and forth every second from being a peach to being a plum. A nectarine is a nectarine all of the time.

The image of a peach is not adequate to describe a nectarine. Neither is the image of a plum. But by imagining both together at the same time, you can get a sense of what a nectarine looks like.

The problem with drawing molecules is similar to the problem above with the nectarine. No single drawing adequately describes the nature of the electron density spread out over the molecule. To solve this problem, we draw several drawings and then meld them together in our mind into one image. Just like the nectarine.

Let's see an example:



Brackets + double arrows

The compound above has two important resonance structures. Notice that we separate resonance structures with a straight, two-headed arrow, and we place brackets around the structures. The arrow and brackets indicate that they are resonance structures *of one molecule*. The molecule is not flipping back and forth between the different resonance structures. The electrons in the molecule are not actually moving at all.

Now that we know why we need resonance, we can begin to understand why resonance structures are so important. Ninety-five percent of the reactions that you will see in this course occur because one molecule has a region of low electron density and the other molecule has a region of high electron density. They attract each other in space, which causes a reaction. So, to predict how and when two molecules will react with each other, we need first to predict where there is low electron density and where there is high electron density. We need to have a firm grasp of resonance to do this. In this chapter, we will see many examples of how to predict the regions of low or high electron density by applying the rules of drawing resonance structures.

2.2 CURVED ARROWS: THE TOOLS FOR DRAWING RESONANCE STRUCTURES

In the beginning of the course, you might encounter problems like this: here is a drawing; now draw the other resonance structures. But later on in the course, it will be assumed and expected that you can draw all of the resonance structures of a compound. If you cannot actually do this, you will be in big trouble later on in the course. So how do you draw all of the resonance structures of a compound? To do this, you need to learn the tools that help you: curved arrows.

Here is where it can be confusing as to what is exactly going on. These arrows do not represent an actual process (such as electrons moving). This is an important point, because you will learn later about curved arrows used in drawing reaction mechanisms. Those arrows look exactly the same, but they actually do refer to the flow of electron density. In contrast, curved arrows here are used only as tools to help us draw all resonance structures of a molecule. The electrons are not actually moving. It can be tricky because we will say things like: "this arrow shows the electrons coming from here and going to there." But we don't actually mean that the electrons are moving; they are *not* moving. Since each drawing treats the electrons as particles stuck in one place, we will need to "move" the electrons to get from one drawing to another. Arrows are the tools that we use to make sure that we know how to draw all resonance structures for a compound. So, let's look at the features of these important curved arrows.

Every curved arrow has a *head* and a *tail*. It is essential that the head and tail of every arrow be drawn in precisely the proper place. *The tail shows where the electrons are coming from, and the head shows where the electrons are going* (remember that the electrons aren't really going anywhere, but we treat them as if they were so we can make sure to draw all resonance structures):

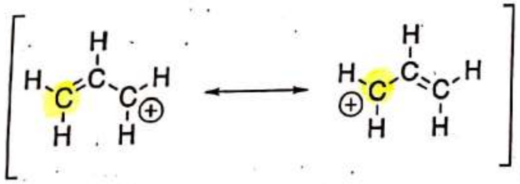
Therefore, there are only two things that you have to get right when drawing an arrow: the tail needs to be in the right place and the head needs to be in the right place. So we need to see rules about where you can and where you cannot draw arrows. But first we need to talk a little bit about electrons, since the arrows are describing the electrons.

Electrons exist in orbitals, which can hold a maximum of two electrons. So there are only three options for any orbital:

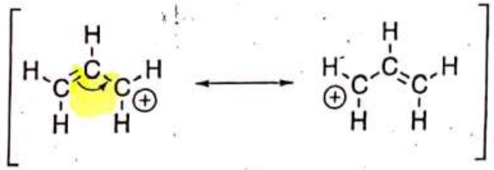
- 0 electrons in the orbital
- 1 electron in the orbital
- 2 electrons in the orbital

If there are no electrons in the orbital, then there's nothing to talk about (there are no electrons there). If you have one electron in the orbital, it can overlap with another electron in a nearby orbital (forming a *bond*). If two electrons occupy the orbital, they fill the orbital (called a *lone pair*). So we see that electrons can be found in only two places: in bonds or in lone pairs. Therefore, electrons can only come from either a bond or a lone pair. Similarly, electrons can only go to form either a bond or a lone pair.

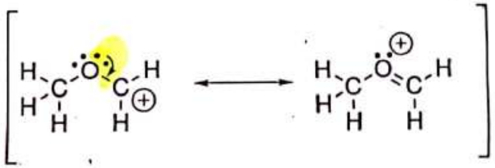
Let's focus on tails of arrows first. Remember that the tail of an arrow indicates where the electrons are coming from. So the tail has to come from a place that has electrons: either from a bond or from a lone pair. Consider the following resonance structures as an example:



How do we get from the first structure to the second one? Notice that the electrons that make up the double bond have been "moved." This is an example of electrons coming from a bond. Let's see the arrow showing the electrons coming from the bond and going to form another bond:

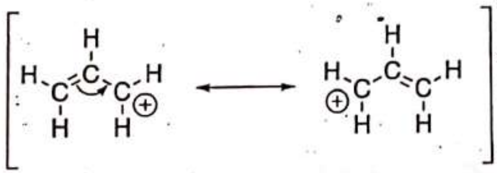


Now let's see what it looks like when electrons come from a lone pair:

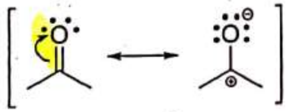


Never draw an arrow that comes from a positive charge. The tail of an arrow must come from a spot that has electrons.

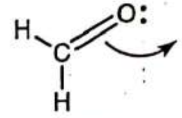
Heads of arrows are just as simple as tails. The head of an arrow shows where the electrons are going. So the head of an arrow must either point directly in between two atoms to form a bond,



or it must point to an atom to form a lone pair.



Never draw the head of an arrow going off into space:



Bad arrow

Remember that the head of an arrow shows where the electrons are going. So the head of an arrow must point to a place where the electrons can go—either to form a bond or to form a lone pair.

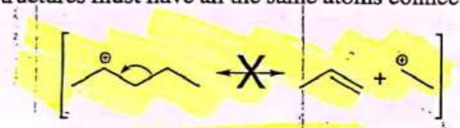
2.3 THE TWO COMMANDMENTS

Now we know what curved arrows are, but how do we know when to push them and where to push them? First, we need to learn where we *cannot* push arrows. There are two important rules that you should *never* violate when pushing arrows. They are the "two commandments" of drawing resonance structures:

1. Thou shall not break a single bond.
2. Thou shall not exceed an octet for second-row elements.

Let's focus on one at a time.

1. *Never break a single bond* when drawing resonance structures. By definition, resonance structures must have all the same atoms connected in the same order.

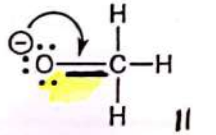


Never break a single bond

There are very few exceptions to this rule, and only a trained organic chemist can be expected to know when it is permissible to violate this rule. Some instructors might violate this rule one or two times (about half-way through the course). If this happens, you should recognize that you are seeing a very rare exception. In virtually every situation that you will encounter, you *cannot* violate this rule. Therefore, you must get into the habit of never breaking a single bond.

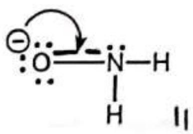
There is a simple way to ensure that you never violate this rule. Just make sure that you never draw the tail of an arrow on a single bond.

2. *Never exceed an octet for second-row elements.* Elements in the second row (C, N, O, F) have only four orbitals in their valence shell. Each of these four orbitals can be used either to form a bond or to hold a lone pair. Each bond requires the use of one orbital, and each lone pair requires the use of one orbital. So the second-row elements can never have five or six bonds; the most is four. Similarly, they can *never* have four bonds and a lone pair, because this would also require five orbitals. For the same reason, they can never have three bonds and two lone pairs. The sum of (bonds) + (lone pairs) for a second-row element can never exceed the number four. Let's see some examples of arrow pushing that violate this second commandment:



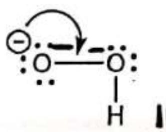
Bad arrow

C ≠ 5 bonds



Bad arrow

N ≠ 4 bonds 1 LP



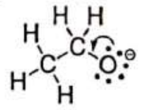
Bad arrow

O ≠ 3 bonds 2 LP

In each of these drawings, the central atom cannot form another bond because it does not have a fifth orbital that can be used. *This is impossible.* Don't ever do this.

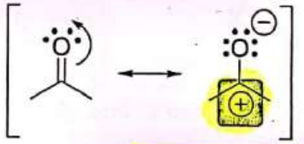
The examples above are clear, but with bond-line drawings, it can be more difficult to see the violation because we cannot see the hydrogen atoms (and, very often, we cannot see the lone pairs either; for now, we will continue to draw lone pairs to ease you into it). You have to train yourself to see the hydrogen atoms and to recognize when you are exceeding an octet:

is the same as



At first it is difficult to see that the arrow on the left structure violates the second commandment. But when we count the hydrogen atoms, we can see that the arrow above would give a carbon atom with five bonds.

From now on, we will refer to the second commandment as "the octet rule." But be careful—for purposes of drawing resonance structures, it is only a violation if we *exceed* an octet for a second-row element. However, there is no problem at all with a second-row element having *fewer* than an octet of electrons. For example:



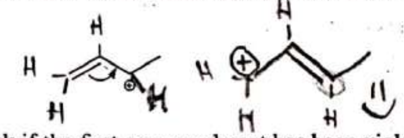
This carbon atom does not have an octet.

This drawing is perfectly acceptable, even though the central carbon atom has only six electrons surrounding it. For our purposes, we will only consider the "octet rule" to be violated if we exceed an octet.

Our two commandments (never break a single bond, and never violate "the octet rule") reflect the two parts of a curved arrow (the head and the tail). A bad tail violates the first commandment, and a bad head violates the second commandment.

EXERCISE 2.1 For the compound below, look at the arrow drawn on the structure and determine whether it violates either of the two commandments for drawing resonance structures:

all good!

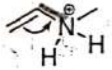


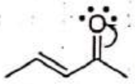
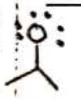
Answer First we need to ask if the first commandment has been violated: did we break a single bond? To determine this, we look at the *tail* of the arrow. If the tail of the arrow is coming from a single bond, then that means we are breaking that single bond. If the tail is coming from a double bond, then we have not violated the first commandment. In this example, the tail is on a double bond, so we did not violate the first commandment.

Now we need to ask if the second commandment has been violated: did we violate the octet rule? To determine this, we look at the *head* of the arrow. Are we forming a fifth bond? Remember that C^+ only has three bonds, not four. When we count the hydrogen atoms attached to this carbon, we see that there is only one hydrogen atom, not two, to give that carbon a total of three bonds. When we move the arrow shown above, the carbon will now get four bonds, and the second commandment has not been violated.

The arrow above is valid, because the two commandments were not violated.

PROBLEMS For each of the problems below, determine which arrows violate either one of the two commandments, and explain why. (Don't forget to count all hydrogen atoms and all lone pairs. You must do this to solve these problems.)

2.2  #2 N ≠ 5 bonds

2.3    O can have 3LP +1 bond

2.4  #2 C ≠ 5 bonds

2.5 

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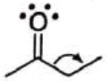
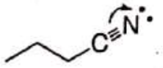
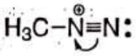
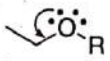
2.7 

2.8 

2.9 

2.10 

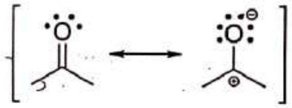
2.11 
$H_3C-\overset{\oplus}{N}\equiv N:$

2.12 

2.4 DRAWING GOOD ARROWS

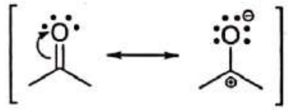
Now that we know how to identify good arrows and bad arrows, we need to get some practice drawing arrows. We know that the tail of an arrow must come either from a bond or a lone pair, and that the head of an arrow must go to form a bond or a lone pair. If we are given two resonance structures and are asked to show the arrow(s) that get us from one resonance structure to the other, it makes sense that we need to look for any bonds or lone pairs that are appearing or disappearing when going from one structure to another. Let's see this with an example.

Say we have two resonance structures:



How would we figure out what curved arrow to draw to get us from the drawing on the left to the drawing on the right? We must look at the difference between the two structures and ask, "How should we push the electrons to get from the first structure to the second structure?" Begin by looking for any double bonds or lone pairs that are disappearing. That will tell us where to put the tail of our arrow. In this example, there are no lone pairs disappearing, but there is a double bond disappearing. So we know that we need to put the tail of our arrow on the double bond.

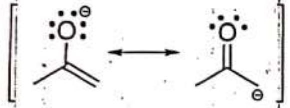
Now, we need to know where to put the head of the arrow. We look for any lone pairs or double bonds that are appearing. We see that there is a new lone pair appearing on the oxygen. So now we know where to put the head of the arrow:



Notice that when we move a double bond up onto an atom to form a lone pair, it creates two formal charges: a positive charge on the carbon that lost its bond and a negative charge on the oxygen that got a lone pair. This is a very important issue. Formal charges were introduced in the last chapter, and now they will become instrumental in drawing resonance structures. For the moment, let's just focus on pushing arrows, and in the next section of this chapter, we will come back to focus on these formal charges.

It is pretty straightforward to see how to push only one arrow that gets us from one resonance structure to another. But what about when we need to push more than one arrow to get from one resonance structure to another? Let's do an example like that.

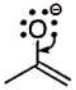
EXERCISE 2.13 For the two structures below, try to draw the curved arrows that get you from the drawing on the left to the drawing on the right:



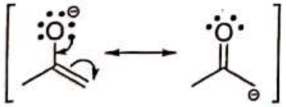
Answer Let's analyze the difference between these two drawings. We begin by looking for any double bonds or lone pairs that are disappearing. We see that the oxygen is losing a lone pair, and the C=C on the bottom is also disappearing. This should automatically tell us that we need two arrows. To lose a lone pair and a double bond, we will need two tails.

Now let's look for any double bonds or lone pairs that are appearing. We see that a C=O is appearing and a C with a negative charge is appearing (remember that a C^- means a C with a lone pair). This tells us that we need two heads, which confirms that we need two arrows.

So we know we need two arrows. Let's start at the top. We lose a lone pair from the oxygen and form a C=O. Let's draw that arrow:



Notice that if we stopped here, we would be violating the second commandment. The central carbon atom is getting five bonds. To avoid this problem, we must immediately draw the second arrow. The C=C disappears (which solves our octet problem) and becomes a lone pair on the carbon. Now we can draw both arrows:

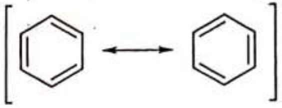


Arrow pushing is much like riding a bike. If you have never done it before, watching someone else will not make you an expert. You have to learn how to balance yourself. Watching someone else is a good start, but you have to get on the bike if you want to learn. You will probably fall a few times, but that's part of the learning process. The same is true with arrow pushing. The only way to learn is with practice.

Now it's time for you to get on the arrow-pushing bike. You would never be stupid enough to try riding a bike for the first time next to a steep cliff. Do not have your first arrow-pushing experience be during your exam. Practice right now!

PROBLEMS For each drawing, try to draw the curved arrows that get you from one drawing to the next. In many cases you will need to draw more than one arrow.

2.14



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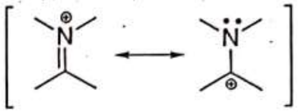

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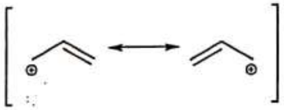

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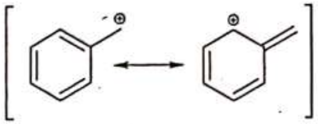

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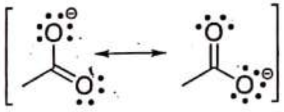

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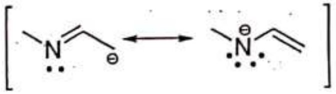
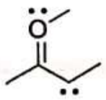


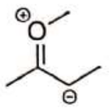
2.5 FORMAL CHARGES IN RESONANCE STRUCTURES

Now we know how to draw good arrows (and how to avoid drawing bad arrows). In the last section, we were given the resonance structures and just had to draw in the arrows. Now we need to take this to the next level. We need to get practice drawing the resonance structures when they are not given. To ease into it, we will still show the arrows, and we will focus on drawing the resonance structures with proper formal charges. Consider the following example:

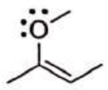
In this example, we can see that one of the lone pairs on the oxygen is coming down to form a bond, and the C=C double bond is being pushed to form a lone pair on a carbon atom. When both arrows are pushed at the same time, we are not violating either of the two commandments. So, let's focus on how to draw the resonance structure. Since we know what arrows mean, it is easy to follow the arrows. We just get rid of one lone pair on the oxygen, place a double bond between the carbon and oxygen, get rid of the carbon–carbon double bond, and place a lone pair on the carbon:



The arrows are really a language, and they tell us what to do. But here comes the tricky part: we cannot forget to put formal charges on the new drawing. If we apply the rules of assigning formal charges, we see that the oxygen gets a positive charge and the carbon gets a negative charge. As long as we draw these charges, it is not necessary to draw in the lone pairs:



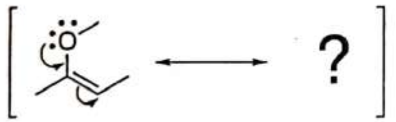
It is absolutely critical to draw these formal charges. Structures drawn without them are *wrong*. In fact, if you forget to draw the formal charges, then you are missing the whole point of resonance. Let's see why. Look at the resonance structure we just drew. Notice that there is a negative charge on a carbon atom. This tells us that this carbon atom is a site of high electron density. We would not know this by looking only at the first drawing of the molecule:



This is why we need resonance—it shows us where there are regions of high and low electron density. If we draw resonance structures without formal charges, then what is the point in drawing the resonance structures at all?

Now that we see that proper formal charges are essential, we should make sure that we know how to draw them when drawing resonance structures. If you are a little bit shaky when it comes to formal charges, go back and review formal charges in the previous chapter. But we can also see where to put formal charges without having to count each time. We saw the common situations for oxygen, nitrogen, and carbon. It is important to remember those (go back and review those if you need to).

Another way to assign formal charges is to read the arrows properly. Let's look at our example again:

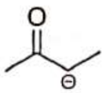


Notice what the arrows are telling us: oxygen is giving up a lone pair (two electrons entirely on the oxygen) to form a bond (two electrons being shared: one for the oxygen and one for the carbon). So oxygen is losing an electron. This tells us that it must get a positive charge in the resonance structure. A similar analysis for the carbon on the bottom right shows that it will get a negative charge. Remember that the electrons are not really moving anywhere. Arrows are just tools that help us draw resonance structures. To use these tools properly, we imagine that the electrons are moving, but they are not.

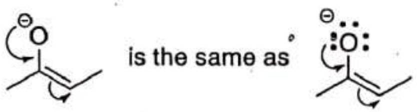
Now let's practice.

EXERCISE 2.20 Draw the resonance structure that you get when you push the arrows shown below. Be sure to include formal charges.

Answer We read the arrows to see what is happening. One of the lone pairs on the oxygen is coming down to form a bond, and the C=C double bond is being pushed to form a lone pair on a carbon atom. This is very similar to the example we just saw. We just get rid of one lone pair on the oxygen, place a double bond between the carbon and oxygen, get rid of the carbon–carbon double bond, and place a lone pair on the carbon. Finally, we must put in any formal charges:



There is one subtle point to mention. We said that you do not need to draw lone pairs—you only need to draw formal charges. There will be times when you will see arrows being pushed on structures that do not have the lone pairs drawn. When this happens, you might see an arrow coming from a negative charge:



The drawing on the left is the common way this is drawn. Just don't forget that the electrons are really coming from a lone pair (as seen in the drawing on the right).

One way to double check your drawing when you are done is to count the total charge on the resonance structure that you draw. This total charge should be the same as the the structure you started with. So if the first structure has a negative charge, then the resonance structure you draw should also have a negative charge. If it doesn't, then you know you did something wrong (this is known as *conservation of charge*). You cannot change the total charge on a compound when drawing resonance structures.

PROBLEMS For each of the structures below, draw the resonance structure that you get when you push the arrows shown. Be sure to include formal charges. (*Hint:* In some cases the lone pairs are drawn and in other cases they are not drawn. Be sure to take them into account even if they are not drawn—you need to train yourself to see lone pairs when they are not drawn.)

2.21

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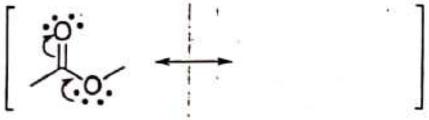

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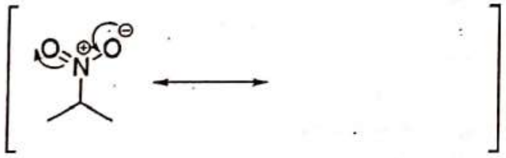
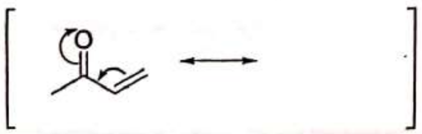


2.28



2.6 DRAWING RESONANCE STRUCTURES—STEP BY STEP

Now we have all the tools we need. We know why we need resonance structures and what they represent. We know about what curved arrows are and where not to draw them. We know how to recognize bad arrows that violate the two commandments. We know how to draw arrows that get you from one structure to another, and we know how to draw in formal charges. We are now ready for the final challenge: drawing curved arrows when we do not know what the next resonance structure looks like. Now that you know when you can and cannot push arrows, you need to practice using arrow pushing to determine by yourself how to draw the other resonance structures.

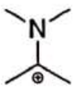
First we need to locate the part of the molecule where resonance is an issue. Remember that we can push electrons only from lone pairs or bonds. We don't need to worry about all bonds, because we can't push an arrow from a single bond (that would violate the first commandment). So we only care about double or triple bonds. Double and triple bonds are called *pi bonds*. So we need to look for lone pairs and pi bonds. Usually, only a small region of the molecule will possess either of these features.

Once we have located the regions where resonance is an issue, now we need to ask if there is any way to push the electrons without violating the two commandments. Let's be methodical, and break this up into three questions:

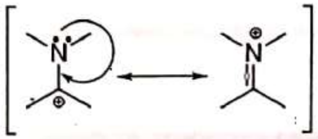
1. Can we convert any *lone pairs into pi bonds* without violating the two commandments?
2. Can we convert any *pi bonds into lone pairs* without violating the two commandments?
3. Can we convert any *pi bonds into pi bonds* without violating the two commandments?

We do not need to worry about the fourth possibility (converting a lone pair into a lone pair) because electrons cannot jump from one atom to another. Only the three possibilities above are acceptable.

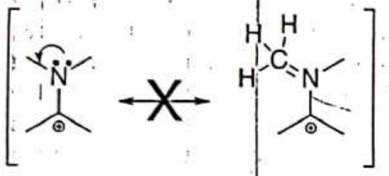
Let's go through these three steps, one at a time, starting with step 1, converting lone pairs into bonds. Consider the following example:



We ask if there are any lone pairs that we can move to form a pi bond. So we draw an arrow that brings the lone pair down to form a pi bond:

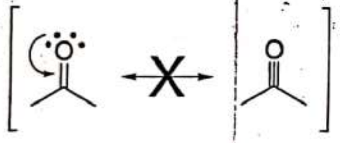


This does not violate either of the two commandments. We did not break any single bonds and we did not violate the octet rule. So this is a valid structure. Notice that we cannot move the lone pair in another direction, because then we would be violating the octet rule:



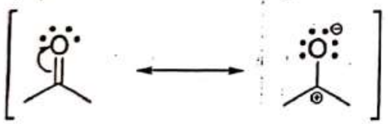
Let's try again with the following example:

We ask if we can move one of the lone pairs down to form a pi bond, so we try to draw it:

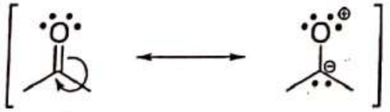


This violates the octet rule—the carbon atom would end up with five bonds. So we cannot push the arrows that way. There is no way to turn the lone pair into a pi bond in this example.

Now let's move on to step 2, converting pi bonds into lone pairs. We try to move the double bond to form a lone pair and we see that we can move the bond in either direction:



or



Neither of these structures violates the two commandments, so both structures above are valid resonance structures. (However, the bottom structure, although valid, is not a significant resonance structure. In the next section, we will see how to determine which resonance structures are significant and which are not.)

For step 3, converting pi bonds into pi bonds, let's consider the following examples:

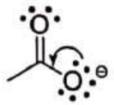
If we try to push the pi bonds to form other pi bonds, we find

No: This violates the octet rule.

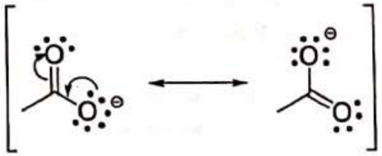
Yes: Does not violate the octet rule.

The top structure violates the octet rule (giving carbon five bonds), and the bottom structure does not violate the octet rule. The arrow on the bottom structure will therefore provide a valid resonance structure:

Now that we have learned all three steps, we need to consider that these steps can be combined. Sometimes we cannot do a step without violating the octet rule, but by doing two steps at the same time, we can avoid violating the octet rule. For example, if we try to turn a lone pair into a bond in the following structure, we see that this would violate the octet rule:

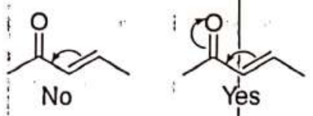


If, at the same time, we also do step 2 (push a pi bond to become a lone pair), then it works:



In other words, you should not always jump to the conclusion that pushing an arrow will violate the octet rule. You should first look to see if you can push another arrow that will eliminate the problem.

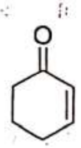
As another example, consider the structure below. We cannot move the C=C bond to become another bond unless we also move the C=O bond to become a lone pair:



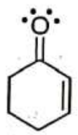
In this way, we truly are "pushing" the electrons around.

Now we are ready to get some practice drawing resonance structures.

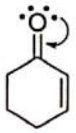
EXERCISE 2.29 Draw all resonance structures for the following compound:



Answer Let's start by finding all of the lone pairs and redrawing the molecule. Oxygen has two bonds here, so it must have two lone pairs (so that it will be using all four orbitals):

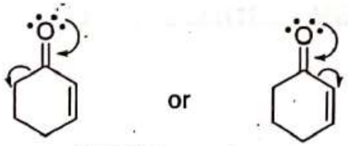


Now let's do step 1: can we convert any lone pairs into pi bonds? If we try to bring down the lone pairs, we will violate the octet rule by forming a carbon atom with five bonds:



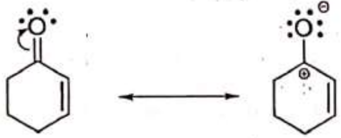
Violates second commandment

The only way to avoid forming a fifth bond for carbon would be to push an arrow that takes electrons away from that carbon. If we try to do this, we will break a single bond and we will be violating the first commandment:

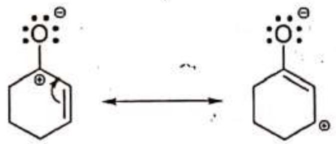


Violates first commandment

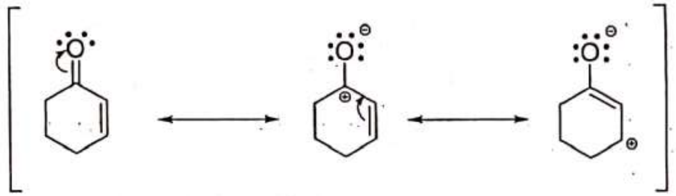
We cannot move a lone pair to form a pi bond, so we move on to step 2: can we convert any pi bonds into lone pairs? Yes:



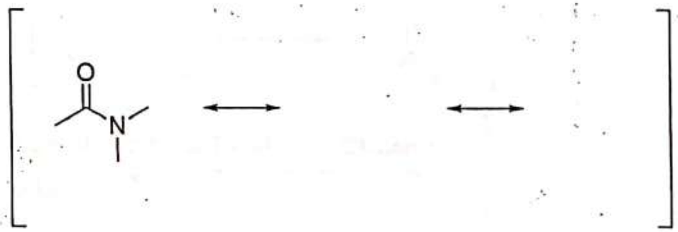
Now we move to step 3: can we convert pi bonds into pi bonds? There is only one move that will not violate the two commandments:



So the resonance structures are



PROBLEM 2.30 For the following compound, go through all three steps (making sure not to violate the two commandments) and draw the resonance structures.



While working through this problem, you probably found that it took a very long time to think through every possibility, to count lone pairs, to worry about violating the octet rule for each atom, to assign formal charges, and so on. Fortunately, there is a way to avoid all of this tedious work. You can learn how to become very quick and efficient at drawing resonance structures if you learn certain patterns and train yourself to recognize those patterns. We will now develop this skill.

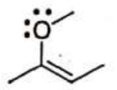
2.7 DRAWING RESONANCE STRUCTURES—BY RECOGNIZING PATTERNS

There are five patterns that you should learn to recognize to become proficient at drawing resonance structures. First we list them, and then we will go through each pattern in detail, with examples and exercises. Here they are:

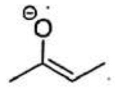
1. A lone pair next to a pi bond.
2. A lone pair next to a positive charge.
3. A pi bond next to a positive charge.
4. A pi bond between two atoms, where one of those atoms is electronegative.
5. Pi bonds going all the way around a ring.

A Lone Pair Next to a Pi Bond

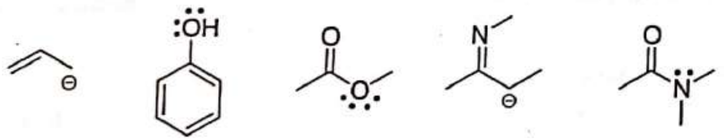
Let's see an example before going into the details:



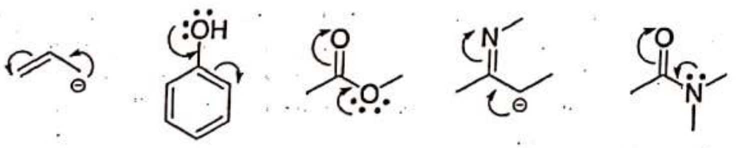
The atom with the lone pair can have no formal charge (as above), or it can have a negative formal charge:



The important part is having a lone pair "next to" the pi bond. "Next to" means that the lone pair is separated from the double bond by exactly one single bond—no more and no less. You can see this in all of the examples below:

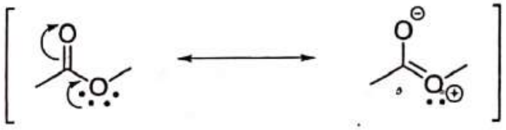


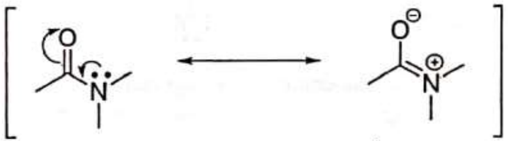
In each of these cases, you can bring down the lone pair to form a pi bond, and kick up the pi bond to form a lone pair:



Notice what happens with the formal charges. When the atom with the lone pair has a negative charge, then it transfers its negative charge to the atom that will get a lone pair in the end:

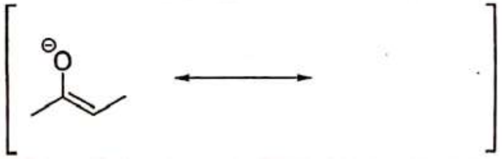
When the atom with the lone pair does not have a negative charge to begin with, then it will end up with a positive charge in the end, while a negative charge will go on the atom getting the lone pair in the end (remember conservation of charge):



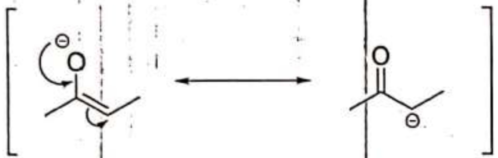


Once you learn to recognize this pattern (a lone pair next to a pi bond), you will be able to save time in calculating formal charges and determining if the octet rule is being violated. You will be able to push the arrows and draw the new resonance structure without thinking about it.

EXERCISE 2.31 Draw the resonance structure of the compound below:



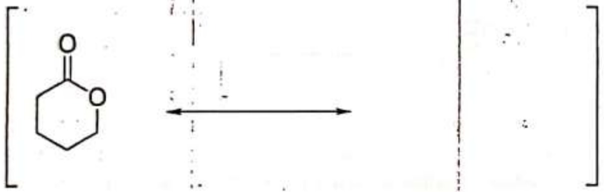
Answer We notice that this is a lone pair next to a pi bond. Therefore, we push two arrows: one from the lone pair to form a pi bond, and one from the pi bond to form a lone pair.



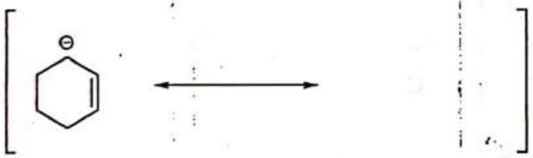
Look carefully at the formal charges. The negative charge used to be on the oxygen, but now it moved to the carbon.

PROBLEMS For each of the compounds below, locate the pattern we just learned and draw the resonance structure.

2.32



2.33



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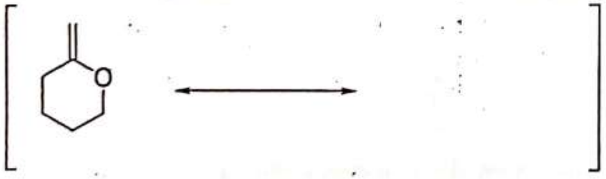

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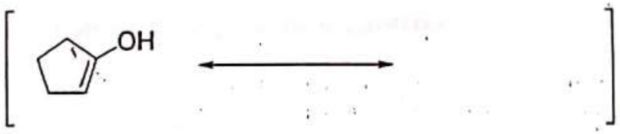
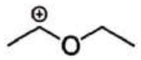


2.39

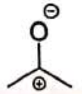
Notice that the lone pair needs to be directly next to the pi bond. If we move the lone pair one atom away, this does not work anymore:

A Lone Pair Next to a Positive Charge

Let's see an example:

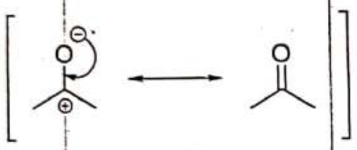


The atom with the lone pair can have no formal charge (as above) or it can have a negative formal charge:



The important part is having a lone pair next to a positive charge. In each of the above cases, we can bring down the lone pair to form a pi bond:

Notice what happens with the formal charges. When the atom with the lone pair has a negative charge, then the charges end up canceling each other:



When the atom with the lone pair does not have a negative charge to begin with, then it will end up with the positive charge in the end (remember conservation of charge):

PROBLEMS For each of the compounds below, locate the pattern we just learned and draw the resonance structure.

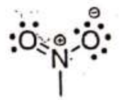
2.40

2.41

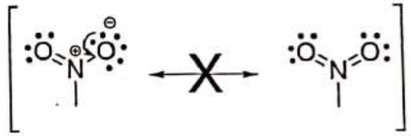
2.42

2.43

Notice that in this problem, a negative and positive charge cancel each other to become a double bond. There is one situation when we cannot combine charges to give a double bond: the nitro group. The structure of the nitro group looks like this:



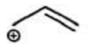
We cannot draw a resonance structure where there are no charges:



This might seem better at first, because we get rid of the charges, but our two commandments show us why it cannot be drawn like this: the nitrogen atom would have five bonds, which this would violate the octet rule.

A Pi Bond Next to a Positive Charge

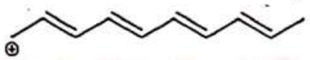
These cases are very easy to see:



We need only one arrow going from the pi bond to form a new pi bond:

Notice what happens to the formal charge in the process. It gets moved to the other end:

It is possible to have many double bonds in conjugation (this means that we have many double bonds that are each separated by only one single bond) next to a positive charge:

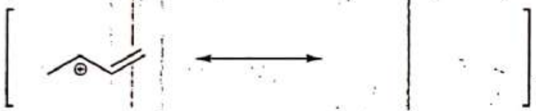


When this happens, we can push all of the double bonds over, and we don't need to worry about calculating formal charges—just move the positive charge to the other end:

Of course, we should push one arrow at a time so that we can draw *all* of the resonance structures. But it is nice to know how the formal charges will end up so that we don't have to calculate them every time we push an arrow.

PROBLEMS For each of the compounds below, locate the pattern we just learned and draw the resonance structure.

2.44



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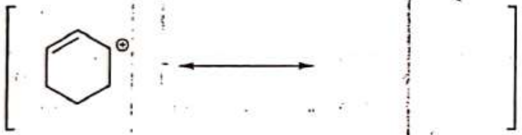

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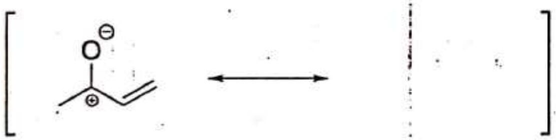
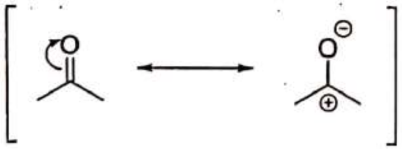


A Pi Bond Between Two Atoms; Where One of Those Atoms Is Electronegative (N, O, etc.)

Let's see an example:

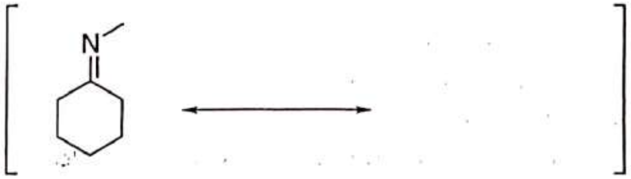
In cases like this, we move the pi bond up onto the electronegative atom to become a lone pair:



Notice what happens with the formal charges. A double bond is being separated int a positive and negative charge (this is the opposite of what we saw in the second pat tern we looked at, where the charges came together to form a double bond).

PROBLEMS For each of the compounds below, locate the pattern we just learne and draw the resonance structure:

2.47



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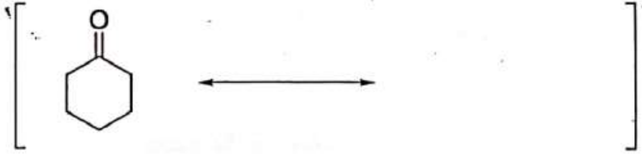

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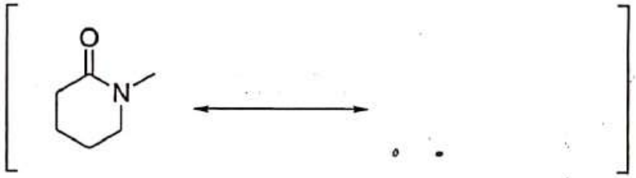
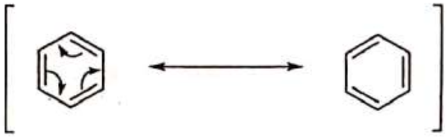


Pi Bonds Going All the Way Around a Ring

Whenever we have alternating double and single bonds, we refer to the alternatin bond system as *conjugated:*

Conjugated double bonds

When we have a conjugated system that wraps around in a circle, then we can a ways move the electrons around in a circle:



It does not matter whether we push our arrows clockwise or counterclockwise (either way gives us the same result, and remember that the electrons are not really moving anyway).

Now we are ready to go back to some problems. Let's try to draw resonance structures again. Only this time, let's try to focus on recognizing some patterns. Look at the examples below, and see if you can recognize any of the patterns we just discussed:

1. A lone pair next to a pi bond.
2. A lone pair next to a positive charge.
3. A pi bond next to a positive charge.
4. A pi bond between two atoms, where one of those atoms is electronegative.
5. Pi bonds going all the way around a ring.

PROBLEMS For each of the following compounds, draw the resonance structures.

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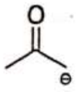
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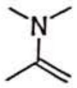
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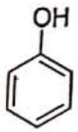

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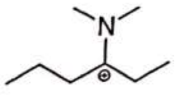
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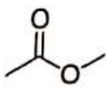
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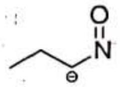
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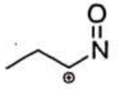
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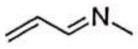
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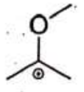
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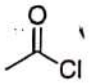
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2.8 ASSESSING THE RELATIVE IMPORTANCE OF RESONANCE STRUCTURES

Not all resonance structures are equally significant. A compound might have *many* valid resonance structures (that do not violate the two commandments), but it is possible that one or more resonance structures might be insignificant. To understand what we mean when we say "insignificant," let's revisit the analogy we used in the beginning of the chapter.

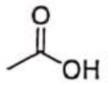
Recall that we used the analogy of a nectarine (being a hybrid between a peach and plum) to explain the concept of resonance. Now, imagine that we create a new type of fruit that is a hybrid between *three* fruits: a peach, a plum, and a kiwi. Suppose that the hybrid fruit that we produce has the following character: 65% peach character, 34% plum character, and 1% kiwi character. This hybrid fruit will look almost exactly like a nectarine, because the amount of kiwi character is too small to have an effect on the nature of the resulting hybrid. Even though this fruit is actually a hybrid of three fruits, nevertheless it will look like a hybrid of only two fruits—because the kiwi character is "insignificant."

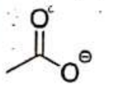
A similar concept exists when comparing resonance structures. One compound might have three resonance structures, but all three resonance structures might not contribute equally to the overall resonance hybrid. One resonance structure might be the major contributor (like the peach), while another resonance structure might be insignificant (like the kiwi). In order to understand the true nature of the compound, we must be able to compare the resonance structures and determine which structures are major contributors and which structures are not significant.

There are two simple rules to follow when comparing resonance structures. At this point, you are probably thinking that it is hard enough to keep track of everything we have seen so far—there are two commandments for how not to push arrows, there are three steps for determining valid resonance structures, there are five patterns, and now there are two rules for determining which resonance structures are significant. The good news is that this is the end of the line. There are no more rules or steps. We are almost done with resonance structures. More good news—drawing resonance structures really is very much like riding a bike. When you first learn to ride a bike, you need to concentrate on every movement to avoid from falling. And you have to remember a lot of rules, such as which way to lean your body and which way to turn the handlebars when you feel you are falling to the left. But eventually, you get the hang of it, and then you can ride the bike with no hands. The same is true here. It will take a lot of practice. But before you know it, you will be the resonance guru, and that is where you need to be to do well in this class.

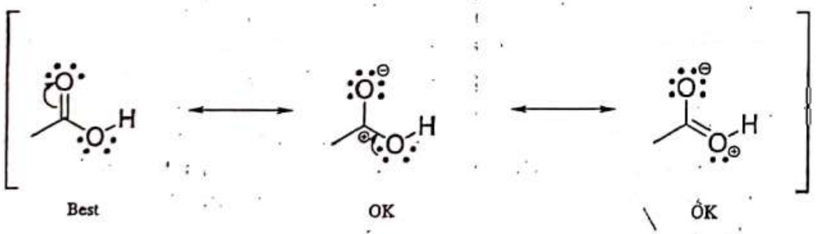
Let's see the two rules for finding which resonance structures are significant:

Rule 1 *Minimize charges.* The best kind of structure is one without any charges. It is OK to have two charges, but you should try to avoid structures that have more than two charges. Compare the following two cases:



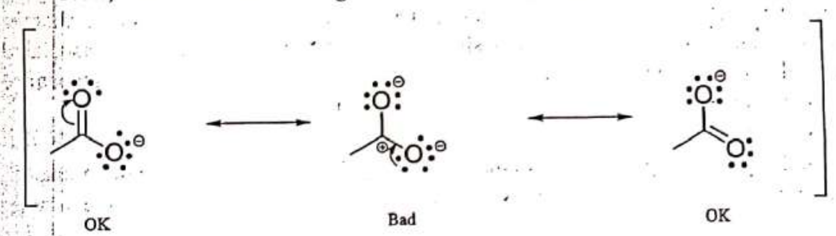


Both compounds have a pi bond between a carbon atom and an electronegative atom (C═O), and both compounds have a lone pair next to the pi bond. So we would expect their resonance structures to be similar, and we would expect these compounds to have the same number of significant resonance structures. But they do not. Let's see why. Let's start by drawing the resonance structures of the first compound:



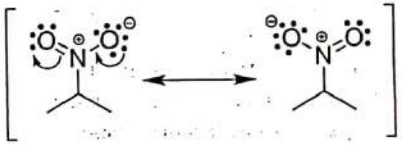
The first resonance structure is the major contributor to the overall resonance hybrid, because it has no charge separation. The other two drawings have charge separation, but there are only two charges in each drawing, so they are both significant resonance structures. They might not contribute as much character as the first resonance structure does, but they are still significant. Therefore, this compound has three significant resonance structures.

Now, let's do the same thing for the other compound:

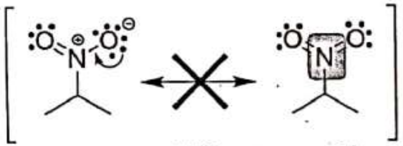


The first and last structures are OK, but the second resonance structure is bad because there are too many charges. This resonance structure is not significant, because it will not contribute much character to the overall resonance hybrid. It is like the kiwi in our analogy above. Therefore, we would say that this compound has only two significant resonance structures.

There is one notable exception to this rule: compounds containing the nitro group ($-NO_2$) will often have resonance structures with more than two charges. Why? The nitro group looks like this:

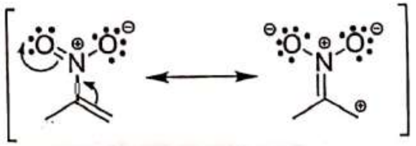


Notice that we have two resonance structures, each of which has charge separation. Even though the molecule has no net charge, nevertheless, we cannot draw a single resonance structure that is free of charge. If we try to do so, we will end up with a structure that violates the second commandment:



Nitrogen cannot have 5 bonds. This violates the octet rule.

Nitrogen cannot have five bonds, so we cannot draw the nitro group without charges. We must draw the nitro group with charge separation. Therefore, the two charges of a nitro group don't really count when we are counting charges. Consider the following case as an example:

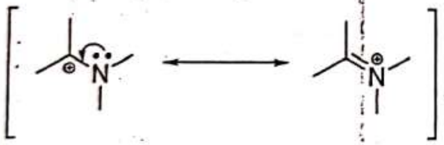


If we apply our rule (about limiting charge separation to no more than two charges), then we might say that the second resonance structure above has too many charges to be significant. But it actually is significant, because the two charges associated with the nitro group are not included in our count. We would consider the resonance structure above as if it only had two charges, and therefore, it is significant.

Rule 2 Electronegative atoms (such as N, O, Cl, etc.) can bear a positive charge, but only if they possess an octet of electrons. Consider the following as an example:

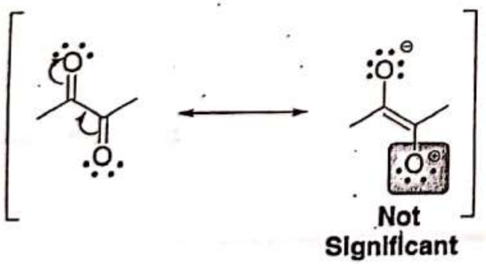
The second resonance structure above is significant, even though it has a positive charge on oxygen. Why? Because the positively charged oxygen has an octet of electrons (three bonds plus one lone pair = 6 + 2 = 8 electrons). In fact, it is not only significant, it is even *more* significant than the first resonance structure. Yes, it is true that the first resonance structure has a positive charge on carbon, which is much better than having a positive charge on oxygen. Nevertheless, the second resonance structure is more significant. Why? In the first structure, the oxygen has its octet, but the carbon only has 6 electrons. In the second resonance structure, both oxygen *and* carbon have their octet. This makes the second resonance structure more significant, even though the positive charge is on oxygen.

Here is another example, this time with the positive charge on nitrogen:



Once again, the second structure is significant (in fact, more significant than the first resonance structure).

When a resonance structure has a positive charge on an electronegative atom, that resonance structure will only be significant if the electronegative atom has an octet. If it does not have an octet, the resonance structure will not be significant. For example, consider the following:



In the example above, the second resonance structure has an oxygen with a positive charge. But this oxygen does *not* have its octet, and therefore, this resonance structure is not significant.

PROBLEMS For each of the following compounds, draw all of the *significant* resonance structures.

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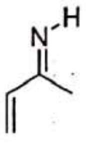

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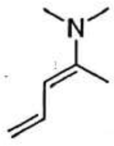

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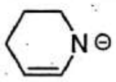

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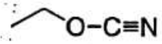

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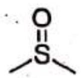

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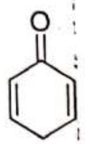

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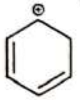

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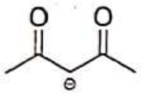

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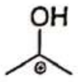

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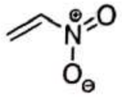

CHAPTER 3

ACID–BASE REACTIONS

The first several chapters of any organic chemistry textbook focus on the structu of molecules: how atoms connect to form bonds, how we draw those connectio the problems with our drawing methods, how we name molecules, what molecu look like in 3D, how molecules twist and bend in space, and so on. Only after ga ing a clear understanding of structure do we move on to reactions. But there see to be one exception: acid–base chemistry.

Acid–base chemistry is typically covered in one of the first few chapters of ganic chemistry textbook, yet it might seem to belong better in the later chapter reactions. There is an important reason why acid–base chemistry is taught so e on in your course. By understanding this reason, you will have a better perspe of why acid–base chemistry is so incredibly important.

To appreciate the reason for teaching acid–base chemistry early in the co we need to first have a very simple understanding of what acid–base chemistry about. Let's summarize with a simple equation:

$$HA \rightleftharpoons H^+ + A^-$$

In the equation above, we see an acid (HA) on the left side of the equilibrium the conjugate base (A^-) on the right side. HA is an acid by virtue of the fact has a proton (H^+) to give. A^- is a base by virtue of the fact that it wants to ta proton back (acids give protons and bases take protons). Since A^- is the base th get when we deprotonate HA, we call A^- the *conjugate base* of HA.

So the question is: how much is HA willing to give up its proton? If very willing to give up the proton, then HA is a strong acid. However, if HA willing to give up its proton, then HA is a weak acid. So, how can we tell w or not HA is willing to give up its proton? *We can figure it out by looking conjugate base.*

Notice that the conjugate base has a negative charge. The real question i stable is that negative charge? If that charge is stable, then HA will be willing up the proton, and therefore HA will be a strong acid. If that charge is not then HA will not be willing to give up its proton, and HA will be a weak aci

So you only need one skill to completely master acid–base chemistr need to be able to look at a negative charge and determine how stable that n charge is. If you can do that, then acid–base chemistry will be a breeze for you cannot determine charge stability, then you will have problems even af finish acid–base chemistry. To predict reactions, you need to know what charges are stable and what kind of charges are not stable.