Introductory Organic Chemistry
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Lecture-03
Introduction to Molecular Orbital Theory Part-2

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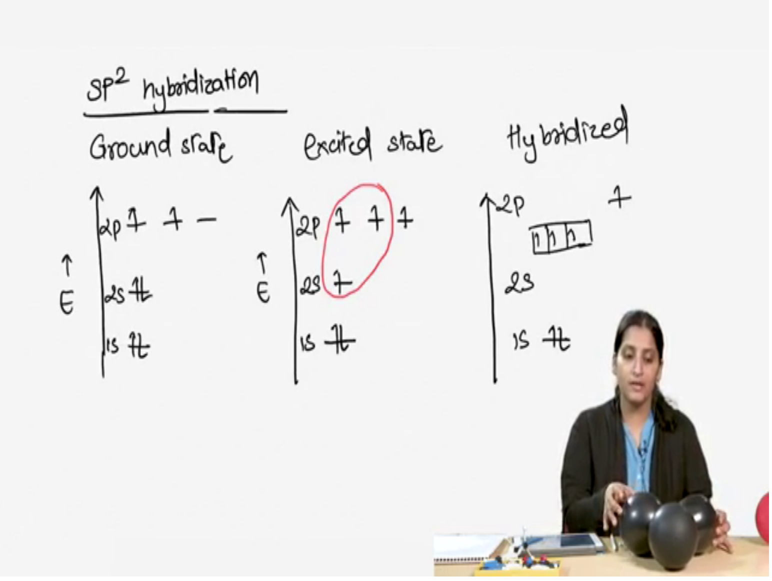

So, one thing to ponder over is why does carbon have to undergo hybridization. If you really think about it, carbon in its ground state can only form three bonds, right because the p orbitals are unoccupied or half filled. Out of that also the bonds formed with the p orbitals are going to be weaker than the bonds formed with the orbitals that have s character in them. So, because the carbon atom is undergoing hybridization, it can now form much stronger bond. So, if you compare this shape of p orbital versus sp3 hybridized orbital; sp3 hybridized orbital is you can imagine has a much larger overlap with that of the 1s than if the bond was just formed with p.

The p orbital is further away from the nucleus. So, the electron in that p orbital is going to be a little away from the nucleus as compared to sp3 hybridized orbital. As a result of all of this what carbon really achieves by doing hybridization is that it can form now stronger bonds or more stable bonds as it undergoes bonding. So, even though carbon atom may have to do this extra work from going from a ground state to the hybridized state; in order to form bonds, remember that extra work is getting paid off by making much stable bonds in the end.

So, that is just like investing small amount right now to get greater returns later on. Okay, but carbon always does not just form single bond. So, you must have seen molecules in which carbon is forming double bonds. So, how does the hybridization of carbon in these compounds look like? So, let's take the example of carbon again and I have drawn here the ground state and the excited state electronic configuration. When carbon is forming a double bond much more likely what it is undergoing is sp2 hybridization.

So, in order to do sp2 hybridization, remember I have to take one of the s orbitals and two of the p orbitals. So, now, let us combine one of these s and two of the p orbitals together to write down the hybridized state electronic configuration of carbon. So, I have 1s orbital which is completely filled, then I have 2s orbital and then I have 2p orbitals.

Now, I have combined 2s with two of the p orbitals to form three of sp2 hybridized orbitals, okay. And remember that one electron that did not take part in hybridization that was there in, let's say, the pz orbital. That pz orbital is still unhybridized and it still has that one electron. So, if you see the electronic configuration in the hybridized state of sp2 hybridization, you can see that there are three sp2 hybridized orbitals and there is also one electron in one of the p orbitals that did not take part in hybridization.

So, now, how does this particular hybridization look like? So, you can imagine that now there are three sp2 hybridized orbitals. Whenever I have three things that have to be placed such that they repel each other in the maximum possible way; in the sense according to the valence shell electron pair repulsion theory if I have to place three orbitals, I will have to place them such that they are kind of at 120 degrees with respect to each other and they are in the same plane.

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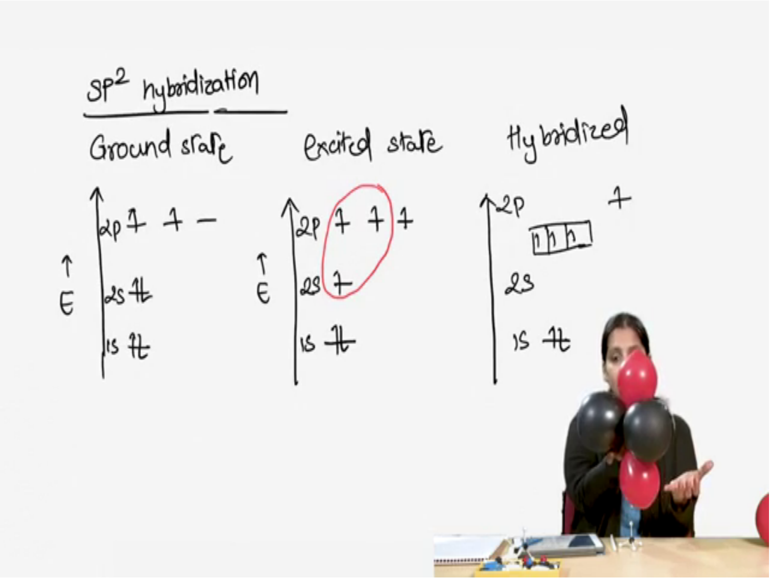

Any other angle is going to create repulsion between two of the low observed orbitals. So, this is what the sp2 hybridized orbitals of carbon look like when it is in sp2 hybridization. But what about that 1p orbital that did not take part in hybridization, that electron is still there and remember that electron will be present and in fact, it will probably occupy a pz orbital that kind of goes above and below this plane, okay.

So, the red lobe here will have that unhybridized; it is the unhybridized p orbital and it will occupy that 1 electron that did not take part in hybridization. So, in the case of ethene, what I have is that each of these sp2 hybridized orbitals will form the sigma bonds and this pz orbital that did not take part in hybridization will take part in the formation of a pi bond. So, now, let us look at the diagram and understand the bonding in carbon-carbon double bonded molecules or let’s take the very simple example of ethene, okay.

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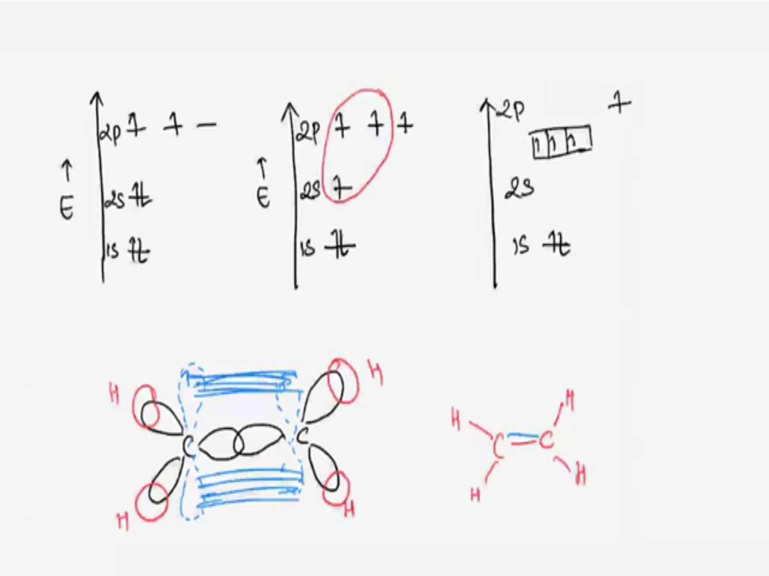

So, now let us look at the bonding in the case of ethene. So, I have a carbon that is the central atom and it has three of these sp2 hybridized orbitals at 120 degrees with respect to each other. Then the other carbon will also overlap with this, with its sp2 hybridized orbitals and each of these will be overlapped with the each of the other two orbitals of carbon, will be overlapped with the 1s orbital of hydrogen, right. So, that is the carbon hydrogen bond, right.

So, this structure is corresponding to something like this so far, right. But remember we also have each of the carbon has the pz orbital that did not take part in hybridization. And that is kind of going above and below the plane of the screen and has one-one electron each, right. So, now, with the sideways overlap of these p orbitals that did not take part in the hybridization, you can have a formation of a pi bond. So, the carbon-carbon double bond exists because you have this sideways overlap of the p orbitals. Okay, so now, there is this sideways overlap of p orbitals and they are going to kind of overlap such that you have carbon-carbon double bond formed.

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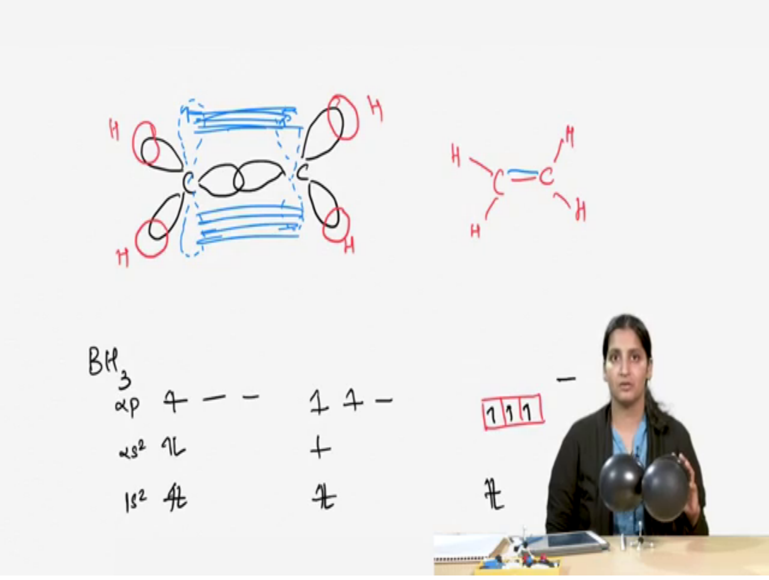

Another example that I want to go over for sp2 hybridization is that of BH3. So, in the case of BH3, remember the central atom is boron and the electronic configuration of boron is 1s 2, 2s 2 and 2p 1, right. Now we have to go to the excited state configuration. So, it will be 1s 2, 2s 1, 2px 1 2py 1, right.

Now if you think about it I need to do an sp2 hybridization so, I need to take one of the s orbitals and two of the p orbitals together and I will form these sp2 hybridized orbitals upon hybridization. And in fact, there is one empty p orbital that did not take part in hybridization, okay. Each of these sp2 hybridized orbitals have one-one electron each. So, you can imagine that this is the boron atom for example, it has these three sp2 hybridized orbitals.

So, you can imagine that this is a boron atom and it has these three sp2 hybridized orbitals in which there is one-one electron each which are going to overlap with the 1s of, let's say, the hydrogen. But what also exists is this empty p orbital that is kind of empty here above and below the plane. So, that's the reason BH3 is more reactive because there is an empty p orbital which can be filled. So, boron can really accept a pair of electrons and can fill this empty p orbital and react in a fashion.

So, BH3 has a particular structure or it is a structure for Lewis acid. So, when we go over the Lewis acids and bases we will understand the reactivity of BH3; but also remember that the structure is strongly correlated with how a particular compound reacts. So, in the case of BH3, you can imagine that since there is an empty space, there is space for some electrons to come and occupy that empty p orbital, okay.

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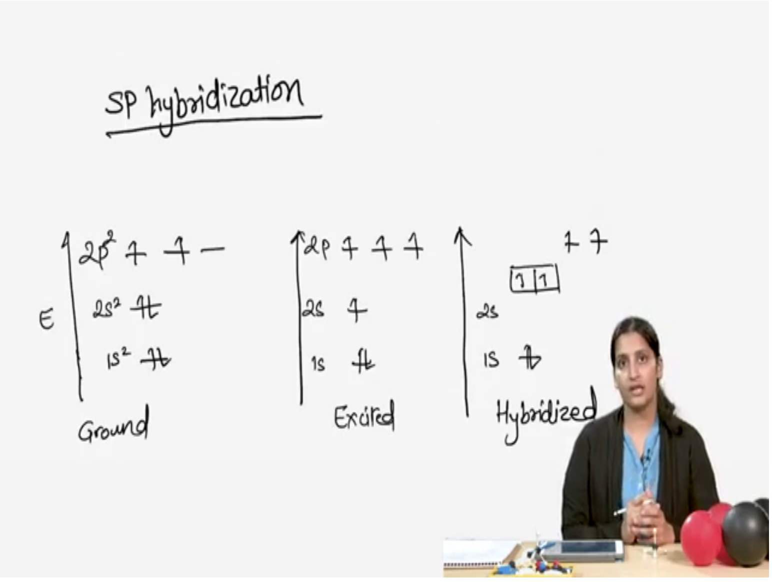

So, now let us go over sp hybridization in which typically you will see carbon forming a triple bond. So, in the case of sp hybridization again, we have to go through the same exercise of ground state to excited state and to hybridized state. So, I have already written the ground and excited state configurations and in the hybridized state as you can see, I can now combine one of the s orbitals and one of the p orbitals because it's sp, right. So, I can only take one of these s and one of the p's.

So, I will take this 2s orbital and let's imagine that we have taken the px orbital. So, what remain with carbon are the py and pz orbital that did not take part in hybridization. So, what I have here? I have two of the orbitals that are sp hybridized and two of the p orbitals that did not take part in hybridization. So, how does the geometry work out in the case of sp hybridization?

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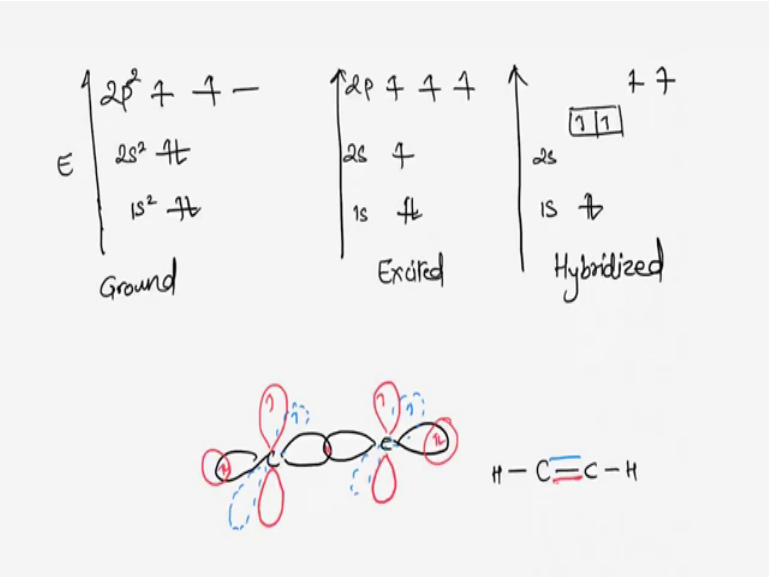

If you think about it; when you have two orbitals that are occupying one electron each, the best way to put them, such that they are farthest apart from each other, is such that they are at 180 degrees with respect to each other. So, anywhere anything closer is going to bring repulsion. So, again according to the VSEPR theory, the best geometry for sp hybridization is such that it is at 180 degrees with respect to each other. So, in the case of let's say acetylene, you have two of the carbons that are sp hybridized.

So, let's look at the orbital overlap in order to see the structure. So, each of these carbons is sp hybridized and what I have here is, their orbitals are at 180 degrees with respect to each other; or you can also call the geometry to be linear. So, it's a linear geometry. So, there is one-one electron from that each of those carbons to form a bond between a carbon and carbon, that is, the sigma bond; sigma covalent bond and then it also has one-one electron in the other side which are overlapped by the 1s orbital of hydrogen. So, what I have here is, hydrogen will overlap this to form a bond between carbon and hydrogen. So, now, I have formed a carbon-carbon sigma bond and two of the carbon hydrogen sigma bonds.

Remember there were those p orbitals that did not take part in hybridization. So, now, what I am going to do is I am going to draw those p orbitals. Now one of the p orbital goes such that it is in the y axis, right. So, if the plane of this particular screen; if we take as the x-axis, then the other p orbital will be in the place of y-axis and they are going to overlap to form a particular pi bond. Whereas the other, one more p orbital will be present in the z-axis which is kind of going above and below the plane which will also have one-one electron each, which are going to form the second pi bond.

So, in the case of acetylene, what we have here is that carbon-carbon sigma bond and each of the carbon is also forming a sigma bond with hydrogen. But what you have is a pi bond between carbon and a carbon atom and also another pi bond as I have shown here to form a triple bond between two carbon-carbon atoms.

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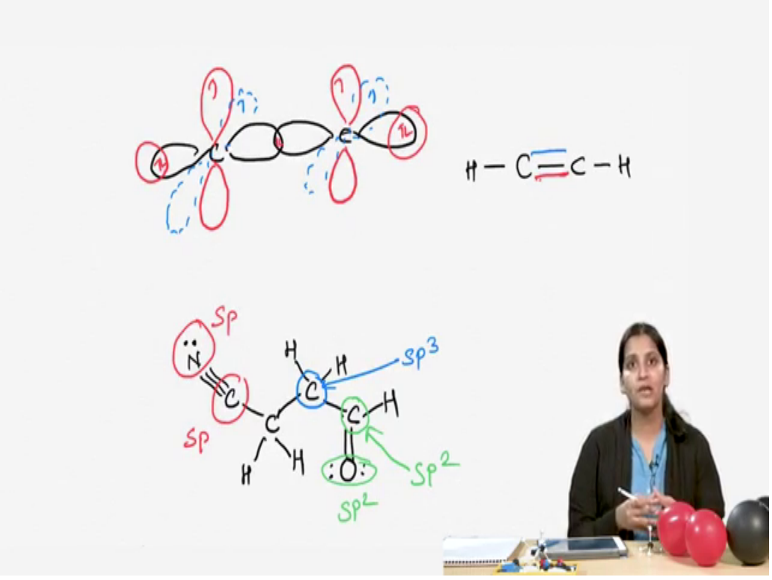

Okay, so we have talked about hybridization, but it is a good thing to quickly be able to tell the hybridization of different atoms in a molecule because remember, hybridization does play a role in the way these molecules react. So, for example, I have taken a molecule here and if you can imagine if we start writing the hybridization of each of the atoms in this particular molecule; you can think that, let’s take some of the atoms. So, let’s look at this particular carbon here. This carbon is forming a triple bond with the nitrogen and a single bond with the other carbon. So in fact, it is forming two sigma bonds and two pi bonds.

Now, in order to achieve the configuration of two sigma and two pi, the carbon has to be sp hybridized. So, this particular carbon will be sp hybridized. On the other hand; if I take this carbon here, this carbon is forming three sigma bonds and one pi bond. In order to achieve three sigma bonds, it needs to have sp2 hybridization. So, I am going to write down sp2 here; and in fact, these middle carbons as you can see are forming four sigma bonds, so they will be sp3 hybridized.

Now, one thing to think about is also the hybridization of heteroatoms. So, whenever we say heteroatoms we are talking about atoms other than carbon and hydrogen. So, we are talking about atoms that are nitrogen and oxygen and chlorine, fluorine etcetera. So, in this case, we have two heteroatoms; we have an oxygen here. So, now, if you think about the hybridization of this particular oxygen, remember the oxygen is forming one sigma bond with the carbon; it has two lone pairs and it has one pi bond. So, you can kind of imagine that the lone pairs are like sigma bonds. So, it is rather forming something similar to three sigma bonds and a pi bond. So, I will say that this particular oxygen is sp2 hybridized.

On the other hand, the nitrogen here is forming one sigma bond with the carbon, it is forming two pi bonds and it has a lone pair. So, again it’s very similar to two sigma bonds and two pi bonds because we can assume lone pair to be corresponding to a sigma bond. So, what I have here, this particular nitrogen will be also sp hybridized. Now, this was a simple trick, but remember there is much more to identifying the hybridization, than just identifying it with the help of the number of sigma and pi bonds. So, we will cover one or two more examples when we have gone over the concept of resonance.

So, once we have done resonance we are gonna revisit how to assign the hybridization of atoms because you will see some of peculiar examples, when resonance takes place, you cannot just use this formula of counting the number of sigma and pi bonds in order to figuring out the hybridization.

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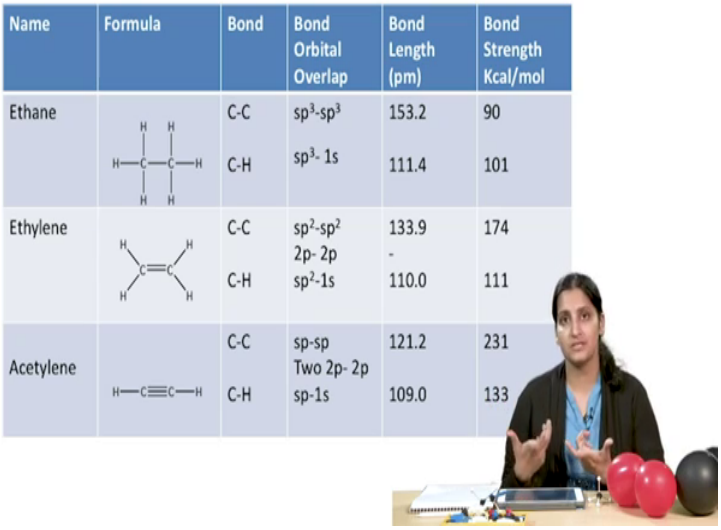

Name	Formula	Bond	Bond Orbital Overlap	Bond Length (pm)	Bond Strength Kcal/mol
Ethane		C-C C-H	sp^3-sp^3 sp^3- 1s	153.2 111.4	90 101
Ethylene		C-C C-H	sp^2-sp^2 2p- 2p sp^2-1s	133.9 - 110.0	174 111
Acetylene		C-C C-H	sp-sp Two 2p- 2p sp-1s	121.2 109.0	231 133

So, now, to summarize the three different types of hybridization we have seen; here is a table that talks about all the characteristics of sp3, sp2 and sp hybridization. So, we have already covered the types of bonds each hybridization can form and we have also covered the geometry, but here is something more that I want to point over.

Now in the case of sp3 hybridization, we have one of the s and three of the p orbitals and we said that together we mash them and form sp3 hybridization. In this case, the total percentage of s character in the case of sp3 is 25 percent and whereas, the p character is 75 percent. So, if you imagine and compare the same thing with sp2 hybridization; in the case of sp2 hybridization, I have 33 percent as character and 66 or 67 percent p character whereas, in the case of sp hybridization, it is 50 and 50.

As you can see the percentage of s character is going on increasing as I go from sp3 to sp hybridization. So, how does this really affect? Remember that the s orbital is different in shape than the p orbital; the s orbital is spherical in shape; the p orbital is dumbbell in shape. So, the shape of sp3 versus sp2 and sp orbitals is also going to change as I am going to change the s character in them.

In fact, as you can imagine the more the s character the shape of this hybridized orbital is gonna go more like a sphere rather than like a dumbbell. So, you can imagine the shape to change; also along with the shape, the bond strength is going to change. So, for example, having more s character in sp hybridization allows that carbon to have a better overlap with the hydrogen and also it allows that particular carbon to have a stronger overlap. So, an sp-sp bond is much stronger as compared to an sp3-sp3 bond; you can see that because of this, the bond length of the sigma bond in the case of sp3 versus sp2 versus sp hybridization also changes and also the bond strength varies with that.

Okay, so far, we have talked about the valence bond theory and we have talked about molecular orbital theory. But are these two theories different or they really go hand in hand? So in fact, in order to understand bonding, we kind of use both these theories and they can be combined together. So, now, let us look at the bonding in methane. According to the valence bond theory, the bonding results because one pair of electron is shared between a carbon and hydrogen atom. And according to the molecular orbital theory we have a molecular orbital formed because of the overlap of the two atomic orbitals.

So, if I really have to talk about the molecular orbitals in the case of methane, what I have to think about is an overlap between sp3 hybridized orbital of carbon and 1s orbital of hydrogen. When these two combine, I can either combine them such that they add or they subtract.

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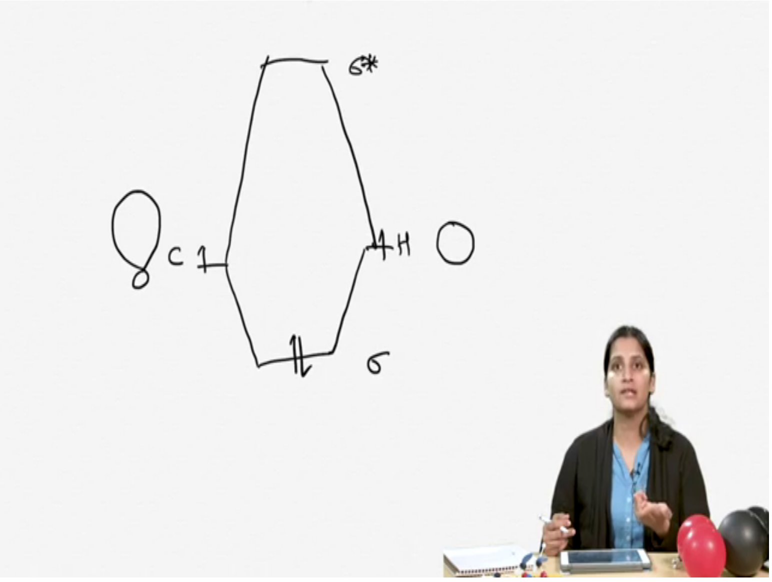

So, in the case of methane if I have to draw the molecular orbital diagram in the case of carbon hydrogen bonding, carbon is sp3 hybridized and hydrogen is 1s orbital. When both of these combined remember that I can form a bonding molecular orbital which is formed because of combination or addition of these two orbitals or I can form an anti bonding molecular orbital which is much higher in energy. So, I have one electron here and one electron here; and in fact, the bonding molecular orbital or the sigma molecular orbital in the case of carbon hydrogen bond is going to be responsible for the stability.

So, when we start filling electrons, we first fill the electrons in this stable sigma molecular orbital and we have no longer electrons left to fill in the sigma star molecular orbital. So, if you think about it, the stabilization that is offered because of this stabilized sigma molecular orbital is comparatively lower than the destabilization that is offered because of filling electrons in the sigma star molecular orbital. And in fact, anytime you fill electrons into the anti bonding orbital of any bond that bond breaks.

So, in order to break this carbon hydrogen bond, what I would have to do is fill in electrons into the anti bonding molecular orbital. And in fact, we will look at some of the reactions henceforth where in we are looking at the molecular orbital theory in which when the anti bonding molecular orbital gets filled, the bond breaks.

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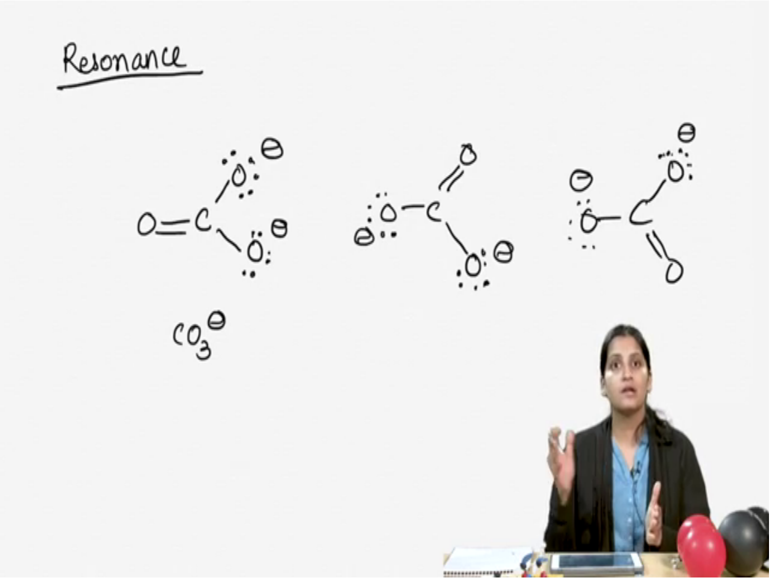

So, as chemists develop a deeper understanding of how a bonding happens or how bondings in various molecules takes place, they soon realized that it is very difficult to represent the bonding in multiple molecules or multiple ions by just one particular Lewis structure. In fact, what they could come up with what multiple Lewis structures for the same molecule or for the same ion.

Here what I have is a carbonate ion and you can see that I have already drawn two structures of carbonate ion such that these two carbonate ion's Lewis structures are different from each other. And even though they are different they are both correct Lewis structure for the carbonate ion. So, in this case now I can in fact, draw one more in which this particular oxygen is double bonded and other two oxygens are single bonded.

So, as you can see that none of these structures are really wrong or in fact, all three of them are correct representation of carbonate ion. So this, kind of puzzled the chemist as to how do we come up with an explanation for these multiple Lewis structures that are possible for a single molecule. Linus Pauling in 1930 gave this concept of resonance through which he tried to explain these multiple Lewis structures. So, now let us look at what resonance is.

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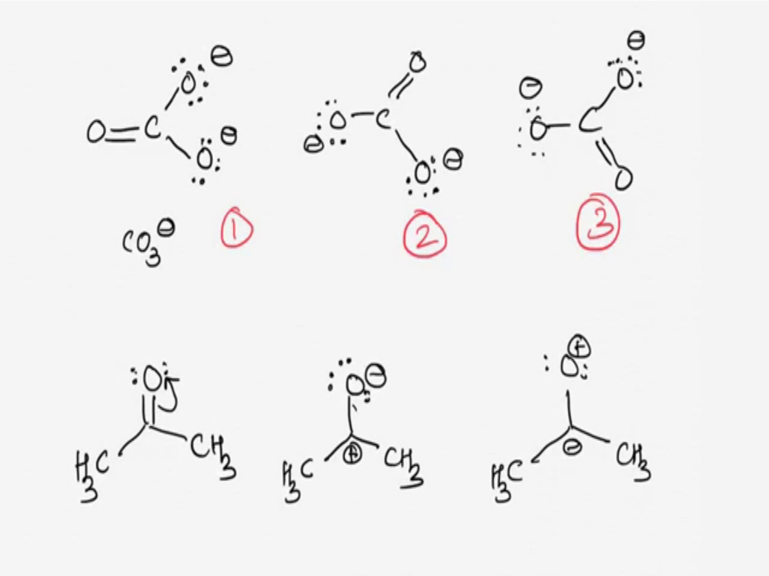

Okay, so according to the resonance theory, it says that whenever there is a case wherein multiple Lewis structures can be drawn which are completely correct for a particular molecule; all of these structures are really contributing towards the net structure of the molecule. So, each of these individual structures will be termed as a contributing resonance structure and when we combine all of them together, what really exists is the resonance hybrid.

So, in a way this particular carbonate ion as I have drawn, is not really existing as the 1st, the 2nd or the 3rd one, but it is rather existing is all three at the same time, okay. And what exist is the hybrid which is kind of a mix of all of these structures.

Now, in order to draw correct resonance structures, one must remember a few rules. So, the first rule of resonance is that I am not allowed to move the atoms. Okay, I am not moving atoms, but what I am allowed to move are the electrons. Okay. And more often these electrons are the lone pair electrons or the pi bond electrons. You more often do not or cannot move a sigma bond, sigma bond electrons because as you move those electrons, you are gonna break the bond, right.

So, you cannot make or break sigma bonds in the case of resonance structures, you cannot move the arrangement of the atoms. So, you cannot change the bonding or the arrangement or the structure of the molecule; what you are allowed to move are these pi bonds or lone pair electrons.

So, now, let us look at a particular resonance structure. Right. So, what I have here is acetone and acetone as you can imagine is one of the most common industrial solvents; it is also used in your nail paint remover. So, acetone here is, you can see that there are various sigma bonds and there is also a pi bond. Now, in order to draw the resonance structure of acetone, I have to only or I can only remove the or change the position of the pi bond.

So, I can change the position such that both of these electrons will now go on that oxygen such that now I have a positive charge on this carbon and a negative charge on the oxygen, okay. If I have to draw the lone pairs, here you go; so, now, it would make sense that oxygen has 3 lone pairs and a sigma bond. So, it should be negatively charged or I can move it the other way around such that the carbon bares the negative charge and the oxygen will be positive in charge, okay. Now, all of these are possible resonance structures of acetone.

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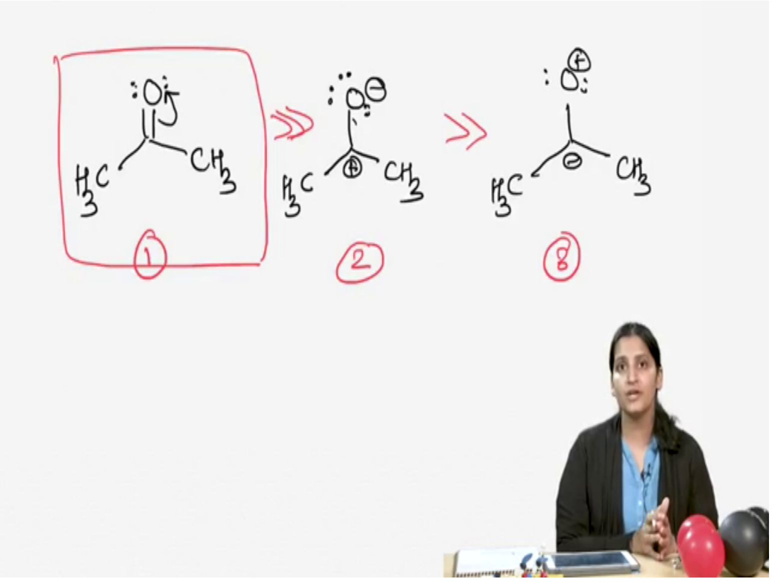

So, remember that all of these are not contributing equally towards the resonance hybrid. If I have to predict which is the more contributing resonance structure, remember there are a couple of rules that we talked about. The first one was the octet rule and octet rule states that whenever you have a complete octet, then that particular atom in that molecule provides a higher stability. So, for example, in the first resonance structure here so, every atom that is each of the carbons and oxygen have a complete octet. So, this one is much more stable than any of the other two resonance structures in which you have an incomplete octet.

In fact, in the second one, carbon does not have a complete octet, in the third one oxygen does not have a complete octet. So, that centrally carbon does not have a complete octet in the second resonance structure. So, both of these are kind of less contributing towards the resonance hybrid and the first one is much more contributing towards the resonance hybrid.

Now, between the second and the third if I have to rank that which one will provide a little more contribution towards the hybrid? I would say that the second one is much more likely to be more contributing than the third one. Why is that? That is because remember in the second resonance structure, the negative charge is on the oxygen. Now, the oxygen is more electronegative. So, it can hold electrons closer to itself and can really stabilize that negative charge better.

On the other hand; in the third one when the oxygen is positively charged and electro negative element like oxygen especially when it bears a positive charge and has an incomplete octet is really really unstable. So, between 2 and 3, I would say that the 2 is much more contributing then the third resonance structure. But remember the first one wherein there are no charges the octet of each atom is complete; you have a much higher likelihood of that contributing more towards the resonance hybrid.

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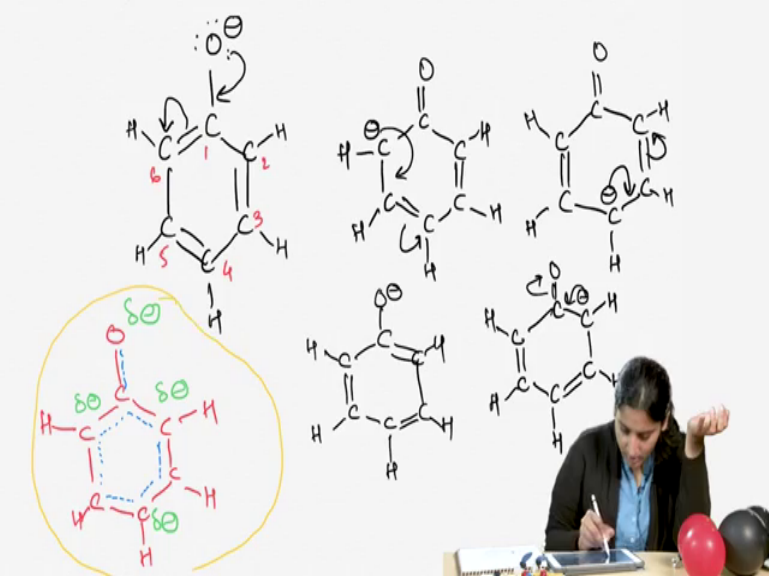

So, I have a phenoxide ion here and phenoxide is basically a conjugate base of phenol. Once we go over acids and bases you will understand the properties of phenoxide. But right now what you can see is that this is a benzene ring on which there is an OH group and in order to draw the resonance structure, remember I can move two electrons at the same time. So, let's say that I move the lone pair electrons of oxygen towards the carbon. Now, that carbon cannot just make one bond extra because it cannot disobey the octet rule. So, what it does is it moves one of these pi bonds on to the other carbon. So, what I give rise to is this particular structure.

Now, in this structure remember, let's number our carbons just for reference. In this new structure carbon number 6 bears the negative charge. I can, in fact, draw many more resonance structures using the same arrow pushing. Remember when you are pushing arrows; if you draw a double headed arrow meaning you are moving both the electrons together.

So, what I have is I can move one more, but again anytime carbon accepts a pair of electrons remember, it cannot make more than four bonds or it cannot have more than eight electrons. So, it has to break one of its bonds. So, that is what we are doing here. So, I will just quickly draw all the resonance structures of this particular phenoxide ion. Okay, and one more we have wherein I move the last one. Okay.

So, now in these all of these resonance structures remember that all of them are contributing towards the resonance hybrid, but I still have not drawn the resonance hybrid. So, there is in fact, one more resonance structure possible and that will give us back our phenoxide ion, right. So, it gives me back my phenoxide ion.

Now, if I have to draw a resonance hybrid for all of these, what I have to think about is first I have to draw the sigma bond framework. The bonds that did not break while I was drawing these resonance structures; I will have to draw them. So, what I am going to draw is a sigma bond framework okay; all the carbon hydrogen sigma bonds also did not break. So, I am going to draw those as well and the carbon oxygen sigma bond also did not break. So, that's the sigma bond framework.

Once I am done with that, what I think about is between the two atoms, any two atoms, is there a double bond in all the structures or is it only existing in some of the structures. So, as you can see between carbon 1 and 2, I have a double bond in one of the resonance structures, but I do not have it for all resonance structures. So, what I will do is I will draw a dashed line between the two carbons. Same goes for the double bonds between carbon 2 and 3.

For example, in the first structure, there is a double bond; in the second structure, there is a double bond, but it does not exist in the 3rd and 4th structure and so on. So, what I will have is a partial line between these carbons because as you can see that the double bond exists between the carbon-carbon such that it exists in all the resonance structures.

Between carbon and oxygen, you have a double bond in some of the structures again and not in some of the structures. So, what I have is a partial double bond, okay. But it is not complete yet. What I also have to think about is which are the charges, or which are the atoms that are bearing the charges. So, oxygen is bearing negative charge in some of the resonance structures, but it does not bear a negative charge in all of the resonance structures. Again when that is the case, I gave a partial negative charge on that oxygen, okay.

If it was a case that it bears a negative charge on all the resonance structures, we would have given a complete negative charge, but right now, it is partial negative for this oxygen. If you see carbon numbers 2, 4 and 6, now are bearing a negative charge in one -one resonance structure each, right. So, what I am going to do is, I am also going to draw partial negative on all of those, right.

So, on carbon numbers 2, 4 and 6, you have a partial negative whereas, carbon numbers 1, 3 and 5, do not have any charges in any of the resonance structures. So, their hybrid kind of looks somewhat like this, wherein now, you have partial lines or dashed bonds in order to show, represent, the movement of the pi electrons. And you also have negative charges or partial negative charges, partial positive charges in some cases to represent that the atom is not having a complete negative or positive charge in all of the resonance structures.