Introductory Organic Chemistry II
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Module 03
Lecture 20
Basics of Carbonyl Compounds

So, in the past two lectures, we have looked at Electrophilic Aromatic Substitution. Now, we will switch our attention to carbonyl compounds, and about 60% of your course of the semester is going to be on this topic. So, we will be looking at how carbonyl components react, and how we can leverage the versatility of this functional group to make complex molecules.

We will be looking at asymmetric synthesis, using this functional group, and so on. So, what I will do in today's topic is that we will try and see how best we can understand the functional group itself. And then we will sort of look at molecular orbital picture of this group, and how that molecular orbital picture can help us understand the various aspects of reactivity.

So, we are going to be using, hybridization or linear combination of atomic orbitals, in terms of description of any compounds, but then we will switch to molecular orbitals when we want to understand certain aspects of stereochemistry and reactivity. So, I think you guys should start getting comfortable with both aspects of theory which can be used to explain the experimental outcome. Of course, please do keep in mind that these are just theories. And they are very useful in helping us understand trends, and helping us reason out experimental outcomes.

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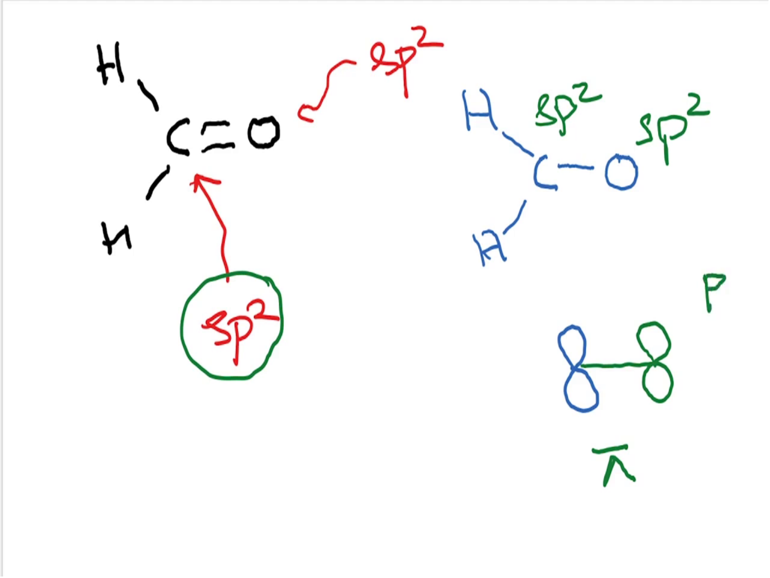

So, let us begin this with Formaldehyde. I think Formaldehyde is one of the simplest components as you can imagine, the carbonyl compound, so, I am just going to draw it out here. So, formaldehyde has a C=O, and it has two hydrogens. And so, if we were to sort of understand, the hybridization of this molecule, the carbon here is going to be sp^2 hybridized.

And the oxygen, is also going to be sp^2 hybridized. And, these two sp^2 hybridization helps us understand the geometry of this molecule, for example, the angle is 120 degrees, and so on. But from a bonding standpoint, see this carbon is first attach to an oxygen through a sigma bond, and of course, these two hydrogens through sigma bonds. And then there is a, this is of course, done by the, the sp^2 carbon and the sp^2 oxygen. And then we have a pi bond. So, the pi bond consists of two of these p orbitals, one on oxygen and one on carbon.

And so, this bond forms the pi bond, which helped us understand the double bond. So, these are things that you already know, but I am just doing a quick recap, so that we can all be on the same page. So, the carbonyl compound has or, the way we understand carbonyl compounds is that the hybridization of the carbon and oxygen is sp^2, and there is one sigma bond between carbon and oxygen, which is through the sp^2 orbitals, and there is one pi bond which is through the p orbitals.

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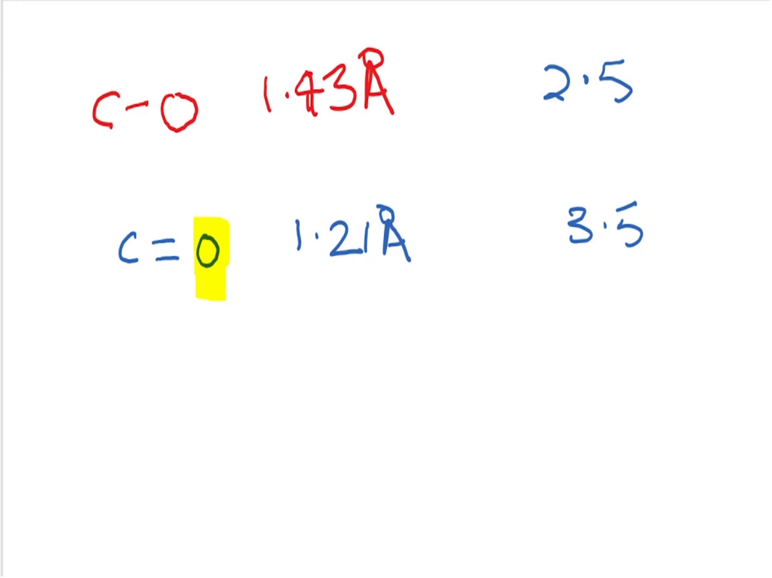

So, now, let us move on to understanding the aspects of carbon and oxygen. So, a typical carbon-oxygen single bond is 1.43 Å and a typical carbon-oxygen double bond is 1.21 Å. And the electronegativity of the carbon is 2.5, whereas the electronegativity of oxygen is 3.5. So, just keep in mind electronegativity is the ability of the nucleus to pull electrons towards itself. And so, oxygen is obviously more electronegative than carbon. And so, that is something that we already know. So, this is just to recap.

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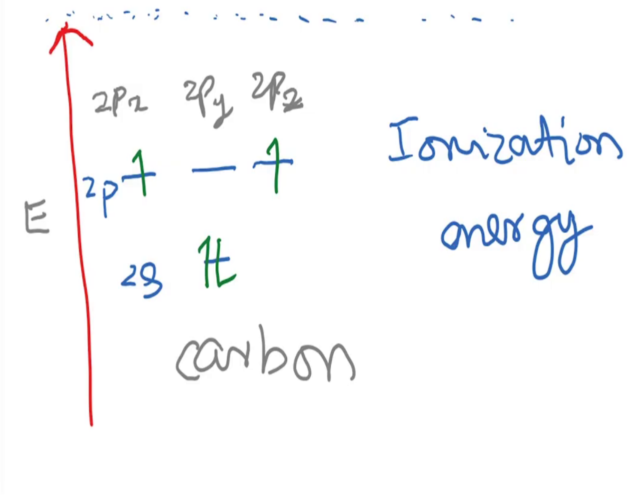

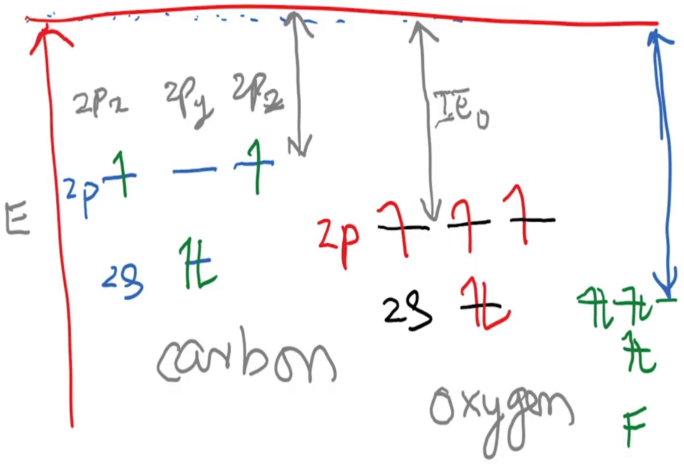

Now, what it also means is that when we start drawing out energy profiles. So, let us look at, for example, the molecular orbital picture of carbon. So, when we start looking at heteronuclear diatomic. It is important to understand the MO picture of this. So, what we need to do is, we need to sort of understand how much energy is required to pull the electron from the outermost filled orbital.

And so, the more electronegative the atom, the more difficult it is to pull it because it is going to be closer to the nucleus. So, with this in mind, let us sort of try and picture the various orbitals of carbon. So, here is carbon. These are the 2s orbitals, and these are the 2p orbitals. So, let us start filling it out. So, there is 1, 2, and then there is 1 over here. And so, this is as you know this is the $2p_x$, $2p_y$, and $2p_z$. So, these are the three p orbitals.

And now, for carbon, let us think about what happens when you pump in some energy. And when you do that, what happens is that one of these electrons goes away that is it is plucked out from the nucleus. So, this is called as the ionization energy. So, this tells us, this is again something that you would have learned many times over in previous courses. But this sort of tells us, how close the electron is to the nucleus. And it also helps us understand electronegativity in one way.

Now, if I have to sort of describe the other similar picture for oxygen, what we would do is since the electronegativity of oxygen is higher. So, if I am going to draw the 2p orbitals for oxygen, so it is going to be something like this. So, here again, this is the 2s. And here are the

2p orbitals for oxygen. And I am just going to fill electrons. And they are these are the same $2p_x$, $2p_y$, and $2p_z$.

And now, if you want to pull an electron out from oxygen, then the kind of energy that you need to spend is actually this. So, when you compare it with carbon, this is the kind of ionization energy of carbon, whereas this is the ionization energy of oxygen. So, now, what it tells you is that this kind of a picture helps us understand that, it is more challenging to pull an electron out from oxygen, compared to carbon.

And so, in order to complete this picture, with whatever space that I have remaining, I am just going to draw out the picture for fluorine, so fluorine is over here. So, again, you have two electrons here. So, the electron activity of fluorine is substantially higher, and the ionization energy is also much higher than that of oxygen, and carbon. So, this kind of a framework helps us understand, where the molecular orbitals or the atomic orbitals are located. And so, when we are trying to draw or construct molecular orbital picture for a double bond, then we need to keep this in mind while doing that.

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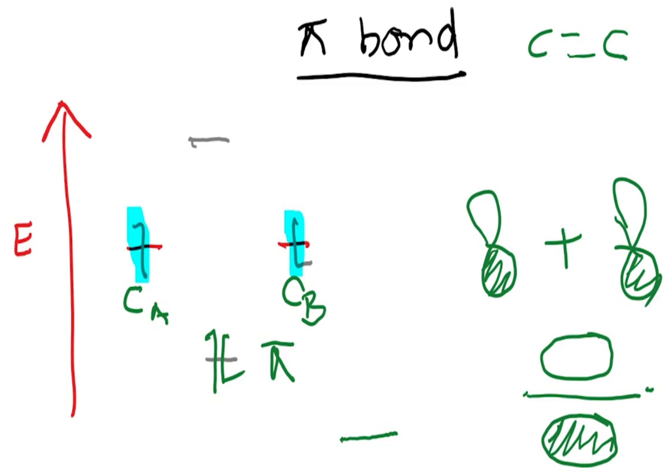

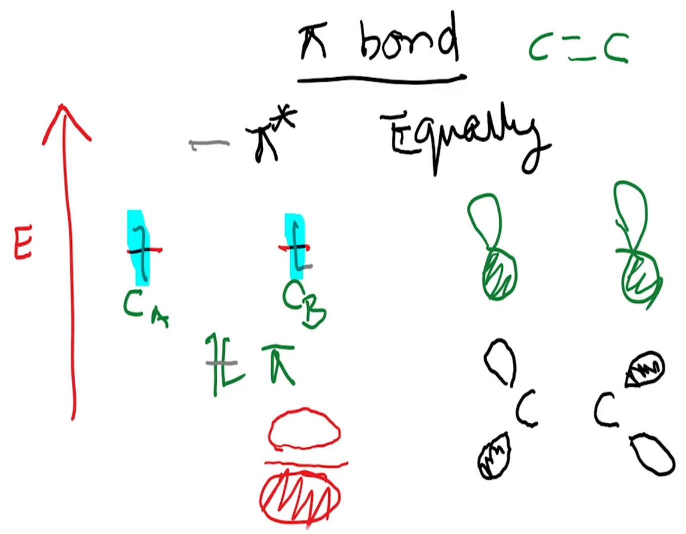

So, for example, when I want to make a pi bond. So, I think we are already quite familiar with sigma bonds, so I am not going to spend time with that. But if I want to construct a molecular orbital picture for a carbon-carbon double bond, then what I would do is, my Y-axis is Energy, and then we have this p orbital for one carbon and then we have a p orbital for another carbon.

So, let us say this is carbon-carbon double bond. So, now this is Carbon A, and this is Carbon B. And now when these atomic orbitals combine, you have one electron each in the atomic orbital. And when these atomic orbitals combine, then you would form a molecular orbital. And this molecular orbital actually has, you know you get two kinds of molecular orbital, as you are all familiar with, one is the bonding, and the other one is the anti-bonding.

And so, both these electrons now are going to be spending, or they going to be populating this bonding molecular orbital over here. And so, this is the pi bond. And so, the bonding molecular orbital, again, as you know is going to be something like this. So, you have the p orbitals are here. And then when they combine, then they are going to form an orbital such as this, between the two nuclei.

So, this is something that, again, you are quite familiar with. So, what you would have is, just to be correct, we need to get the right sign for the atomic orbitals. So, this is going to be a pi bond. And now, similarly, when you want to form antibonding orbitals, then the way you would combine these antibonding orbitals is the following manner. So, I am just going to erase this, so that now we can use the same picture as much as possible.

So, I am just going to draw it again here. So, this is going to be my bonding orbital. And now let us look at the anti-bonding situation. So, when you subtract out, I know when they combine and form the anti-bonding orbital, then you are going to get a node that is formed. And so, this is the carbon atom, and this is another carbon atom. And so, the way in which the antibonding orbitals are going to look like is something like this.

So, you have much better pictures in the textbook. And so, just to be clear, these are going to be the signs of this bonding orbitals. So, this is called us π^* or anti-bonding orbital. So, very important here to understand that both the carbons contribute equally. So, they are essentially identical in all respects. So, they contribute equally to the ensuing molecular orbital.

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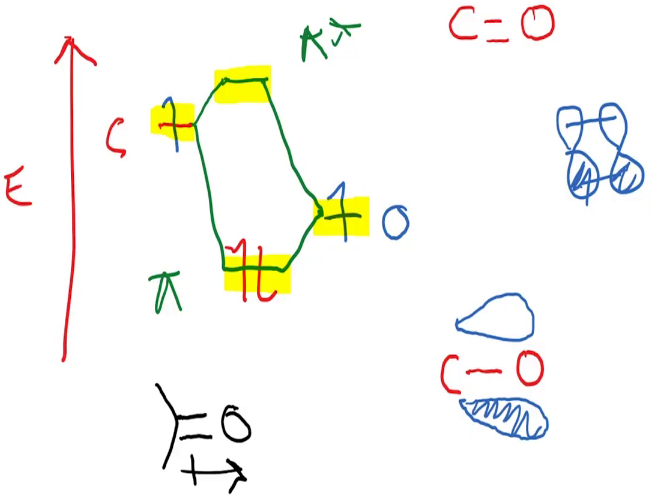

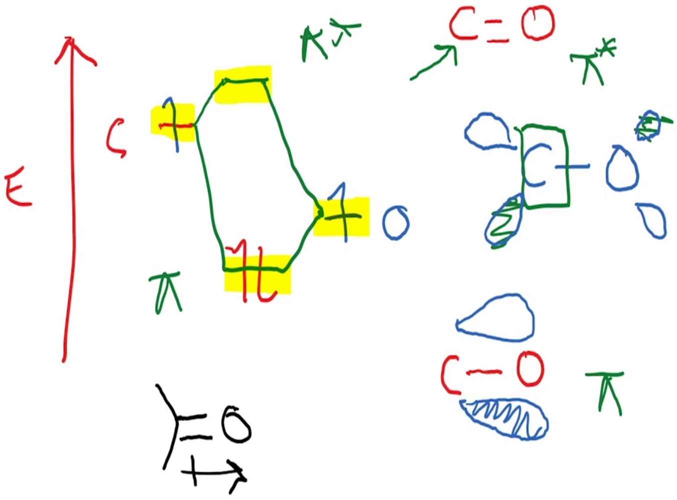

And now let us try to, sort of construct a similar picture for the carbonyl, C=O. So, again, a lot of reactivity of carbonyl will depend on the pi bond. So, let us now only worry about the pi bond. So, let us see, we draw the molecular orbital picture over here. So, as I told you earlier, carbon is here, and oxygen is here. And again, we need to concern ourselves only with the p orbital, which has one electron each, that is, now we shall assume that both of these p orbitals are going to combine and form a pi bond.

And so again, just to remind you, this is the p orbital, and they combine and they give two molecular orbitals, which are denoted as π and π^*. So, here is the way we understand this. So, you are going to combine these two orbitals and produce, two molecular orbitals, so this is the π, and this is the π^*. And so, both electrons are going to be populating the pi bond.

And now, if you want to understand how this pi bond is going to look like, it is very interesting, because the π^*, for example, has a greater contribution from carbon, whereas the pi bond has a much greater contribution from oxygen, because the character of the pi bond is going to be dictated by the bonding orbital of the pi bond, the pi orbital is going to be influenced greater by oxygen. So, this is something that we can reason out, trying to measure the polarity of the molecule.

And when we draw out carbonyl, typically, what we do is, when we measure the dipole moment, the dipole moment is in the direction of the oxygen. So, this sort of helps us put this in perspective. Now, let us come to the shape of the orbitals. So, when you draw carbon and oxygen, if I am going to measure, I am going to study the contribution from oxygen is greater.

And so, the molecular orbital will look something like this. There is going to be a much greater contribution from oxygen compared to carbon. So, therefore, this is something that we need to understand. And the corollary to this is that you will have a much greater contribution from carbon when it comes to the antibonding orbital. So, let me just erase this, so that we can draw it out over here.

So, here is the carbon-oxygen antibonding orbital, so if I have to draw it like this, it will be over here and then over here, and then this is much smaller compared to the carbon-carbon double bond. So, there are two important messages here. So, the π^* has a greater contribution from carbon, whereas the π has a greater contribution from oxygen.

Now, one of the meanings of this is that when you want to break the carbon-oxygen bond, so what you would do is, you would need to fill in the carbon-oxygen π^*, which is the anti-bonding orbital, and therefore, the more reactive centre here would be the carbon. So, this molecular orbital picture helps us understand the reactivity of a carbonyl functional group, the way we have been used to in terms of the experiments that we do, for example, when we add anything across a carbonyl double bond, the carbon invariably ends up reacting. And therefore, this MO picture helps us put these results in perspective.

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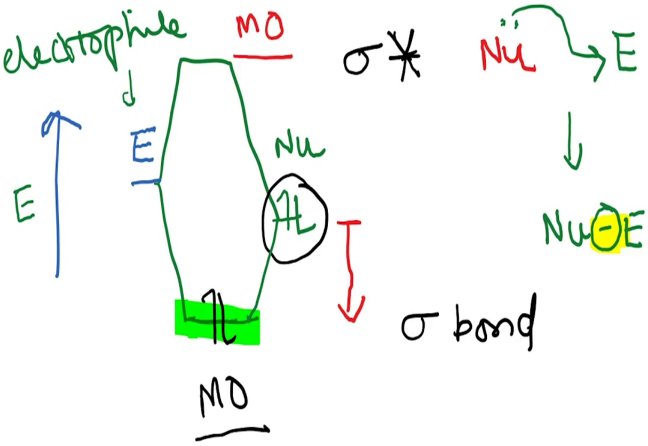

So, now, given that we have understood how the molecular orbital picture of a carbonyl compound looks like, or a carbon functional group looks like. Now let us look at, some molecular orbital picture of a reaction between an electrophile and a nucleophile. So, as we discussed, so MO theory is very powerful, it helps us understand many aspects of what goes on in a reaction, for example.

So, if we would generate an energy profile diagram. So, an electrophile, which I am going to call as E, has particular energy levels such as this. And so, if you recall, a nucleophile, and an electrophile, react in the following manner, so E is over here. So, there is either a pair of electrons or a negative charge, attacking the electrophile, E can be E^+ or neutral electrophile.

And that is going to give you a new bond between Nu and E. And, there is going to be charge involved here. If Nu^- is there, then it is going to become a neutral species. And you also sometimes have a leaving group, and so on and so forth. But essentially, this is the new bond that is being formed between the nucleophile and the electrophile.

So, bond formation involves a pair of electrons. So, coming back to this molecular orbital picture. So, if this is energy, and this is the electrophile, E here denotes an electrophile. And now, if you want to understand this, in terms of how it reacts with a nucleophile, so assume that the nucleophile has to have a pair of electrons, so this is a pair of electrons for the nucleophile. And so, which I am going to denote as Nu.

And now, if we were to construct MO diagram, so when these two mix, that is this electrophile and nucleophile interact, what is going to happen is you are going to have two new sets of orbitals being formed. One is this and the other one is this. So, this kind of an interaction happens during a bond formation. And now this pair of electrons, which was here is now going to form a new molecular orbital.

And this molecular orbital is going to, basically this denotes the sigma bond, for example. And if this is a sigma bond, and then this becomes sigma star. So, all of this, you guys know, so I am just going to quickly go through this. But the important point to note here is that this energy that is now sort of the gain in stability, by loss of energy is what people understand as a driving force for this reaction.

So, the reaction between a nucleophile and an electrophile can result in the formation of a bond. And this bond, is going to have energy that is lower in energy. I mean, there is going to be stabilization of the electrons during this process. So, therefore, for reaction to occur, electrons have to move. And energy differences are important.

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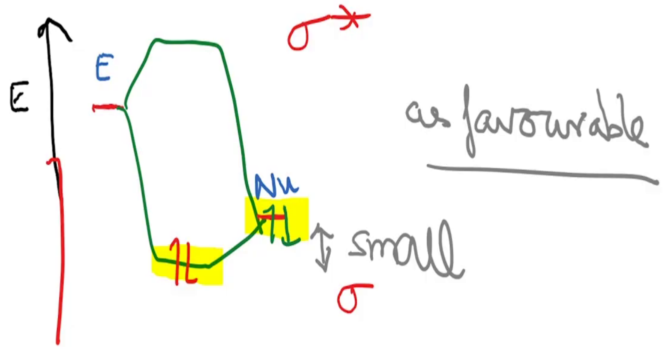

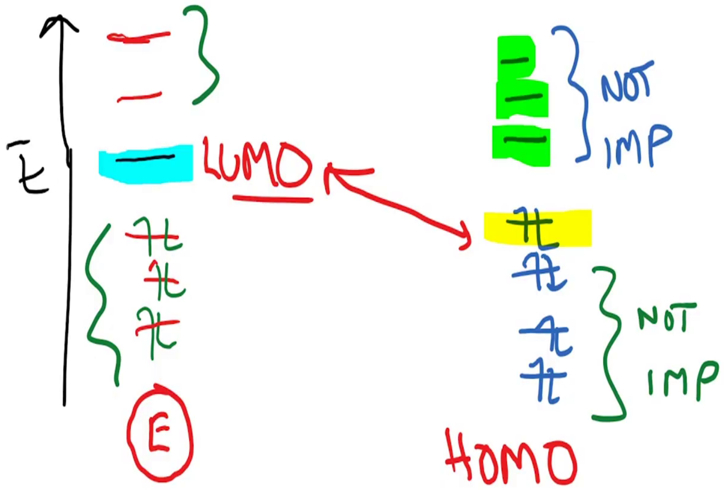

Now, let us think about several situations that can occur. So, situation number one is in your energy profile. So, let us say the electrophile is over here. And the nucleophile is very stable, there is a huge difference, huge gap in the energy. So, this is the electrophile. And this is the nucleophile. So, imagine that this is going to be the kind of gap that we are looking at. So, the nucleophile, as we discussed, has a pair of electrons, and the electrophile is going to be an empty orbital.

And now, when you draw the molecular orbital picture, you are going to see that it is going to look something like this. So, and therefore, your pair of electrons is going to be here, and let us assume that this is a new sigma bond, this is going to be a sigma star, and so on. So, if I look at this picture, I see that there is clearly some stabilization that is being afforded because if I compare these two energy levels, the sigma molecular orbital is lower energy, but this gap is quite small.

So, based on this analysis, what we can sort of suggest is that although there is a gain in energy, the gain in energy is quite small. And therefore, this may not be as favourable as something which has a greater gain, or a greater gain in stability. So, this is not as favourable. And so, it may or may not occur, it is probably likely that this kind of a reaction does not occur.

Now, if you consider the opposite situation, or not opposite situation, but another situation where the energy levels are quite close to each other, then when you form new molecular orbitals, then you have a substantial gain in stability. So, therefore, the matching of levels of energy between the electrophile and nucleophile, are going to be quite important. In general, when we are looking at the reaction of two separate, I mean, of an electrophile and a nucleophile, what we need to look at is something like this.

So, if I draw the Y-axis over here, and this is energy, then, what we need to really consider is that in the electrophile, there would be several energy levels. So, this is going to be the, let us say many energy levels, and each of these energy levels is going to have a pair of electrons. So, the pair of electrons I am going to denote in the following manner. And they are also going to be many unoccupied orbitals, which are going to be higher in energy.

So, the most important one, is this, it is called the lowest unoccupied molecular orbital or LUMO. So, it is important for you to understand this that there are several, you know orbitals which are vacant and there are a set of several orbitals which are filled. When you are considering from the electrophile standpoint, the most important orbital is the LUMO, which is the lowest unoccupied molecular orbital.

Now, if I were to construct a similar picture for the nucleophile, the nucleophile also may have several occupied orbitals. And there are going to be several other orbitals which are unoccupied, so they are free. So, these are all free orbitals, that is they are vacant. So, again, these are not important. And in this case, the most important orbital that we need to concern ourselves with is this one, which is the highest occupied molecular orbital.

So, this interaction between the highest occupied molecular orbital, and the lowest unoccupied molecular orbital is the one that we are always going to be worried about. So, again, just to repeat, these are all filled orbitals, but again, they are not important. And, in the case of the electrophile, the filled ones are clearly not important. But the unfilled ones with higher energy are also not important.

So, this helps us simplify the treatment. And it helps us put a lot of things in perspective, because now we need to concern ourselves only with the lowest unoccupied molecular orbital and the highest occupied molecular orbital. Now, coming back to the question of the carbonyl.

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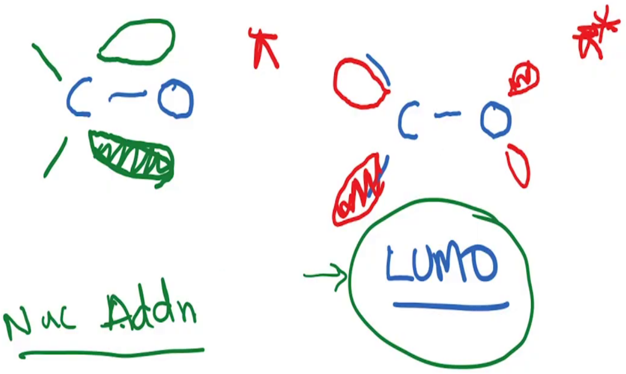

Now, let us go back and look at the molecular orbital picture that we have constructed. So, we saw that there is a carbon, and then there is an oxygen. And that is a sigma bond. And you have, let us say, in case of Formaldehyde, you have another couple of sigma bonds with hydrogen here. And we saw that the π orbital was skewed towards oxygen. And it was looking something like this. And this is the occupied orbital, which is the π orbital.

So, this would be considered the highest occupied molecular orbital. And now, if you look at the corresponding LUMO. So, I am just going to draw it here. The LUMO is going to look something like this. So, you have electron density is going to be, or the orbital density is going to be higher on the carbon when compared to the oxygen. And that is something that we already reasoned out in the previous lecture. And so, these are going to be your π^* orbitals.

So, this is important because now the π^* is the lowest unoccupied molecular orbital. So, when we are looking at carbonyl chemistry, we invariably are concerned about the lowest unoccupied molecular orbital when we are looking at nucleophilic substitution or addition reactions.

And the reason being that when a nucleophile attacks, the nucleophile already has a pair of electrons. And so, the nucleophile is looking for unoccupied molecular orbital, which it can dump its electrons in and it can break another bond and form a new bond. So, therefore, we need to be concerned in the case of the carbonyl with the lowest unoccupied molecular orbital.

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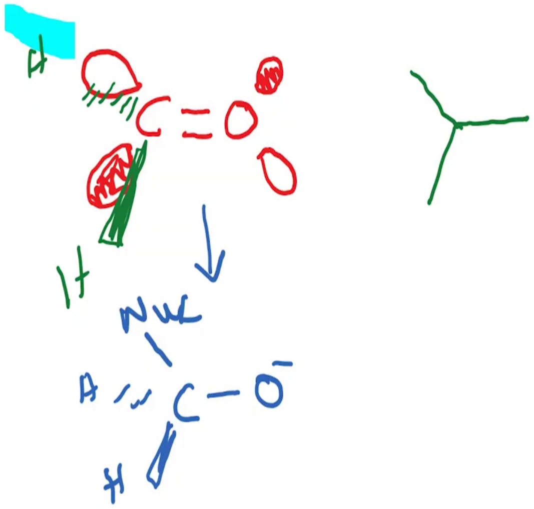

So, just to sort of put this back in perspective. So, here is your C=O, and here is the lowest unoccupied molecular orbital or the π^* and just to be correct, we have to sort of shade this, so that we show the correct sign. And if I have to look at this from the standpoint of geometry, then this is going to be one of the hydrogens and this is going to be another hydrogen.

So, therefore, the C=O is in the plane and this π^* orbital is over here. So, therefore, when this attacks, when a nucleophile attacks, the nucleophile approaches from here and it starts to bond with the π^* orbital and this results in the breaking of the carbon-oxygen π bond and you end up with a new bond between the carbon and oxygen.

So, this is how we would understand the reaction, or nucleophilic addition towards carbonyl compound. So, just to repeat, in order to form a bond here, we need to break or we need to add electrons to an anti-bonding orbital or the π^* orbital. And once the π^* is filled, that results in breaking of the π bond and then the electrons are moved towards the oxygen. So, this is how we try and understand how nucleophilic addition happens on a carbonyl compound.