Introductory Organic Chemistry
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Lecture - 24
Arrow Pushing Mechanism in Organic Chemistry

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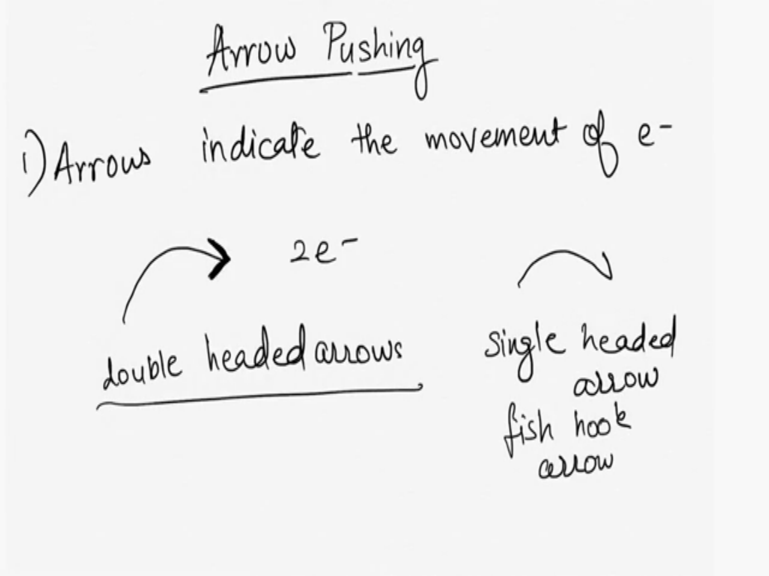

Arrow Pushing

1) Arrows indicate the movement of e-

Mastering reaction mechanisms is a very critical step we all must do to understand the mechanism rather than just simply memorizing it; remember there are really hundreds of Organic Chemistry reactions. So, if you have to remember each and every one of them it is gonna be very difficult. So, we are going to now use tools to really understand the mechanisms. Being able to rationalize reaction outcomes on the basis of small number of, like fundamental principles, it will provide you with the toolbox that you can use to apply it to unknown reactions.

So, if you even know completely unknown reaction comes in front of you, you can apply the toolbox to really predict the products of the reaction by knowing the character of the reactants. I always say that every reactant has a particular character, it likes to react in some conditions; it does not like to react in other conditions. So, every now and then you are going to have to really know the character of a reactant as I call it.

So that you can imagine that when this particular reactant reacts in a different reaction how would it really work with. It also helps us to group reactions according to their nature or according to the mechanisms. So, understanding the mechanism is going to be very important for us. So, to develop an understanding of reaction, what do chemists do? If I ask you this question; chemists really treat it like solving a puzzle.

So, they begin by first using combination of experience and intuition to really come up with the possible ways or the possible several steps of the mechanism that might occur for the overall chemical transformation okay. So, they have now tried to hypothesize how the reaction could be taking place, how each step of the reaction could be taking place such that the overall transformation makes sense. After this what they do is they test each of these proposed steps, okay.

So, we have now laid down the steps, now the next rule is to really test each of these proposed mechanism steps by designing and carrying out experiments that provide the experimental observations, that will allow us to either exclude one of these steps or really corroborate them. So, like either you can justify the step or you have to exclude it if it does not work well.

So, what chemists do is they first hypothesize the test and then perform experiments to justify the steps. Nowadays you also have modern computational methods to allow the detailed prediction of mechanistic pathways and the computational methods allow it much more accurately than ever before. But, even with the computation the results must be still compared with experiment for the confirmation. So, overall a mechanism gets established by showing that it is consistent with each and every test that was ever devised.

And, it really does not mean that we have found out the true nature of all reaction mechanism. Every now and then if a new evidence comes to place, we have to check whether the mechanism holds true or not. And, we have to change our mechanism if it does not work well, okay. So, there have been cases when a new experimental evidence was obtained, people have modified the generally accepted mechanism or even for sometimes even discarded it in favor of an alternative mechanism proposed.

Before, we go on to consider the reactions or reaction mechanisms; one question you want to ask is why do we really go through the trouble of establishing a reaction mechanism. And, why you should spend more time understanding them and more time learning the reaction mechanisms. So, one of the reasons is that mechanisms allow us to really put the information, the chemical information that we have into a really good framework okay. So, for example, if

I know how a reagent reacts with alkenes, how a particular reagent reacts in a reaction with an alkene; I can pretty much predict how the same reagent can react with some other alkene, completely unknown alkene, right.

Or more so, this whole exercise of figuring out how a mechanism works well is really an intellectual satisfaction that helps us to accurately reflect the behavior of chemical systems. Like have we figured out how a particular reaction takes place or not is it's like a puzzle and chemists love solving puzzles. A mechanism that is consistent with all that is known about reaction can be used to even make predictions about chemical interactions. So, experiments can be designed to test these predictions.

Thus, reaction mechanisms provide a way not only to organize knowledge, but also to create new knowledge. And so, as we begin our journey into chemical reactions with this chapter, I want to focus first on what are mechanisms and how to really understand mechanisms rather than really memorize them. The ability to write an Organic Chemistry mechanism really is really the key for doing well in this course, okay.

Organic chemists used techniques called as electron pushing or even we call it as arrow pushing to depict the flow or the movement of an electron okay. So, arrow pushing helps chemists keep a track of the way in which electrons and their associated atoms really redistribute as bonds are made or bonds are broken in a reaction okay. So, I am gonna go over some essential rules to draw this electron pushing okay.

So, the first rule is that arrows indicate the movement of electrons, not of charges, but they are really indicating how electrons from each atom are moving while the reaction is taking place; okay. So, there are two types of arrows you will see in this course; one is a regular arrow or I call it as a double headed arrow and the double headed arrow indicates that 2 electrons are moving at a time. So, this indicates 2 electron movement. One of the ways we show it is that this arrow has two heads whereas, a single headed arrow is going to show the movement of 1 electron moving, right.

So, in this case this is also sometimes called as a fish hook arrow right. Right now more often in this course you will see the double headed arrows being used, because more often an electron pair will do that attack. Because, you need 2 electrons to form a bond, a new bond that's why more often you will see the double headed arrows taking place. But, there are reactions in which we will see the use of single headed arrows and these are really useful for the radical reactions. When we go over some of the mechanisms that use radicals or involved with radical reactions, you will see the use of this fish hook arrows as we go, okay.

So, typically in a chemical reaction both the electrons and the atoms are going to change position as we break and make new sigma and pi bond, right. Arrow pushing is used to keep a track of the movement of the electrons involved in each step of their transformation, okay. Because, electrons are really located in the orbital surrounding atoms; when bonds are formed or broken the electrons are really the key players that take part in this transformation. Movement of electrons is necessarily accompanied by the movement of associated atoms.

I cannot just move electrons; I have to move the atom that is bound to it right or the atom that really possesses those electrons, okay. So, this leads to our second rule of arrow pushing which states that arrows are never used to indicate the movement of atoms directly ok. The arrows only show the atom movement indirectly as a consequence of electron movement.

So, which second rule is really just telling you the seriousness of the first rule right which means that it even if you see an atom moving in an organic chemistry reaction, we don't show it as the atom moving; we show as the electrons moving because, the electrons are associated with the corresponding atom, okay.

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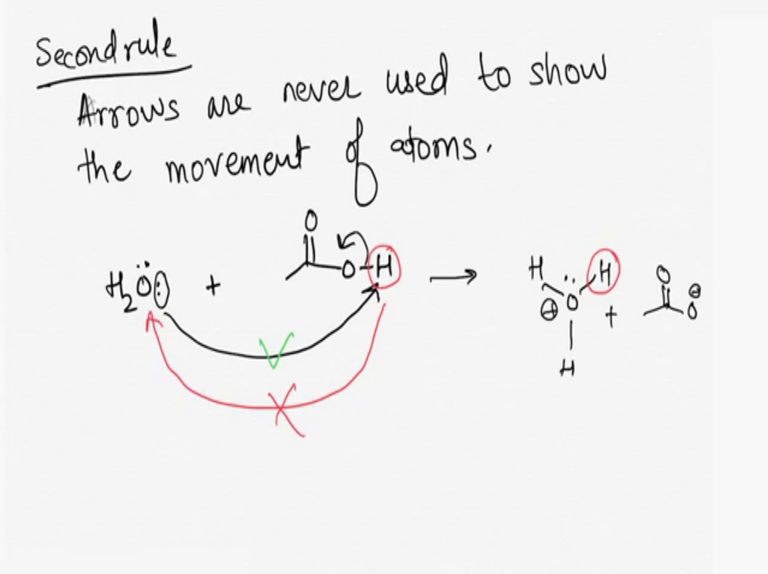

Second rule

Arrows are never used to show the movement of atoms.

So, let me just write down the second rule here, okay. So, if I have to give an example here, if let say water is going to act as a base and it is going to grab a proton from acetic acid, okay.

Now, in an acid base reaction we saw how we push arrows, but I want to go over it again. The arrows need to start from the electron pair and need to go towards the proton right and what we saw is that this is how the reaction takes place.

So, we have formation of H_3O^+ and acetate ion, remember even though I want to show that this particular Hydrogen moved from here to water; I did not show the arrow such that this Hydrogen going here. This kind of arrow would be wrong, the correct kind of arrow is from the electrons to the electron sink which is what our third rule really state is that arrows always start at an electron source that is an electron rich species which may be something like a pi bond or it could be something like a negative charge or lone pair of electrons and, it always ends at an electron sink. Now, electron sink meaning something that is deficient of electrons okay. So, this is going to be a positive charge or it is going to be a proton. For example, in case of HCl, the Hydrogen is really an electron sink because the Hydrogen is already having a partial positive charge, because Chlorine is pulling electrons away from that Hydrogen. So, the arrows always starts from an electron source and end at an electron sink, okay.

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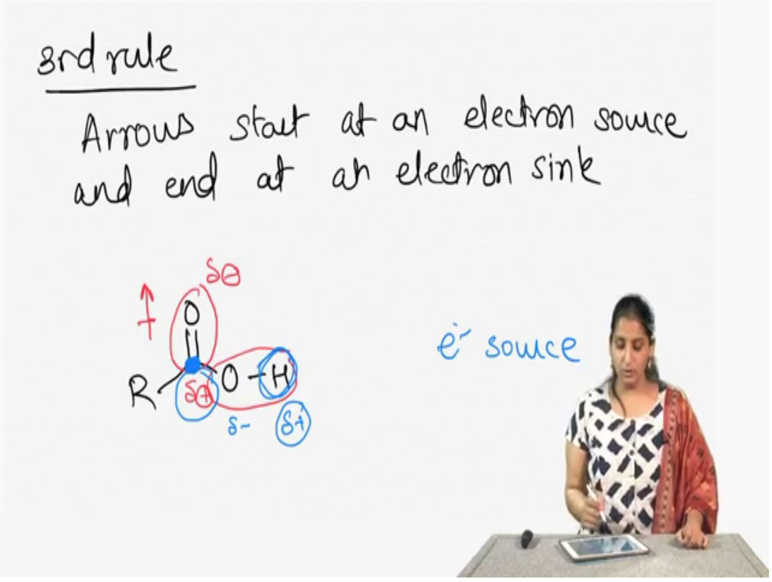

3rd rule

Arrows start at an electron source and end at an electron sink

So, this also means that we can draw arrows from the nucleophile to the electrophile. Nucleophile is something that loves a positive charge to an electrophile which is like an electrons sink, but never the other way round. So, I can never begin an arrow from a positive charge that would be wrong to draw. Learning to identify the characteristics sources that is the electron sources and characteristics electron sinks in various functional group is the key to learning Organic Chemistry reaction mechanisms okay.

So, I am going to just a couple of functional groups here and we are going to see how to use our knowledge of atomic bonding to really predict where is the electron source and predict where is the electrons sink in a particular functional group. So, as I said let us take the first one as our carboxylic acids RC=OOH is the functional group.

Now to think about it, this C=O is really the key player here; Oxygen being really electron negative as compared to Carbon is pulling electrons away from that Carbon and what you see as a result of which is that there is a strong dipole being created. And, Oxygen really pulls all the electrons away from Carbon; so, Oxygen gets partial negative charge and Carbon here will get a partial positive charge okay.

The same thing here between this Oxygen and Hydrogen bond, you will see that the Hydrogen will have a partial positive charge and the Oxygen will be partial negative charge. Again the reason is that you are going to have much more electronegativity difference between Oxygen and Hydrogen and Oxygen wants to keep the electrons with itself, okay.

So, now that I have drawn this kind of a map for carboxylic acids, what you see is that anytime the molecule has to react with an electron source, okay; two kind of reactions can happen first of all. So, let’s take an electron source and that electron source is going a see these two charges, it is going a see the partially positive charges that are there in the molecule.

So, either the electron source can attack this Hydrogen and grab it in an Acid-Base reaction or the electron source can attack this particular Carbon here and attack it such that you do something called as a nucleophillic attack okay. Now, don’t go into the details, but what is important is that looking at this particular structure, I can predict how this particular molecule will react with something like an electron source.

So, with any nucleophile I can predict how it will react. Now, the acid-base reaction will always happen in much more faster than the nucleophillic attack and that is something we have seen in the acid-base chapter. But, remember that looking at the structure I get some insight into the reactivity.

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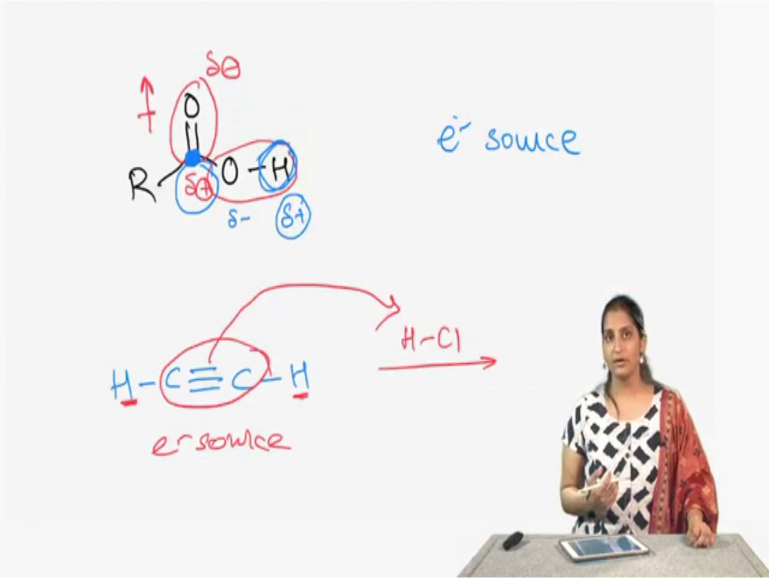

Let’s take one more example and now I am going to take the example of a Carbon-Carbon triple bond, okay. So now, here what I am going to do is I have a Carbon-Carbon triple bond in the molecule which means that there are a lot more electrons present there. There are so many pi electrons which can be easily broken as compared to sigma bond electrons.

So, when I look at this particular molecule I see an electron source; right. On the other hand I don’t see per say an electrons sink here, although these hydrogen here are going to be little delta positive, but not really a lot; right. So, there is not a significant electron sink here, but I do see an electron source in the molecule. So, when this particular compound reacts with for example, HCl the double bond will go and attack the partial positive charge on the proton okay.

So, what you are saying is that the prediction of many of the most important electron sources and sinks really comes down to lessons concerning the differences in the electronegativity, right. So, that’s why when we started the course we did the thorough understanding of bonding and also a thorough understanding of the electronegativity, right. If you are ever confused just go back to the first chapter and try to use that knowledge to predict the reactivity of various molecules.

Okay, which brings me to my fourth rule, okay so, the fourth rule says that bond breaking will occur to avoid overfilling valency of an atom serving as the electron sink. What does this mean? This really is nothing, but our octet rule and we have said these multiple times that

Octet Rule rules. So, anytime you want to put more electrons into the electron sink than it can really hold; it's gonna break one of the bonds. And really try to obey the octet rule, if it is a second row element or Hydrogen will just have to have one bond right.

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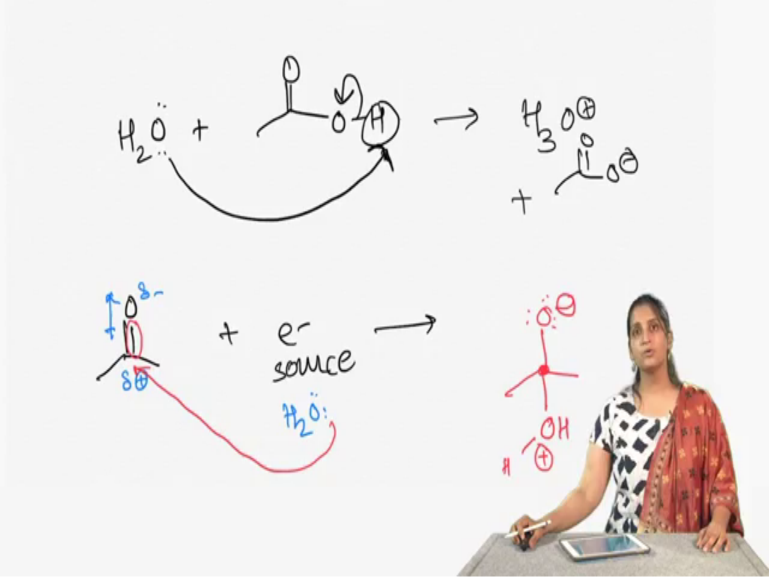

So, let's take an example; for example, if I take just the same example that we just saw. When water attacked this particular proton, this proton did not want to form two bonds at the same time right, because it really breaks its valency. As a result of which it breaks the bond with the Oxygen. So, bond breaking will occur, if that Hydrogen does not want to form two bonds at the same time. You will see multiple examples like this, more often you will see protons getting transferred.

So, for example, in this case the proton gets transferred on the water, right and you form an acetate ion, but you will see protons being transferred, you will also see protons being taken away, right. So, for example, if I just have to draw the reverse reaction that acetate ion will have to grab a proton from that water, right, because, while it is grabbing that proton, that proton will break a bond with that Oxygen, okay.

Let me take one more example where this is even much more evident. So, now let's go over the next example. Now, in the next example I have been given a ketone, acetone and an electron source. Again to predict the reactivity of acetone, I am just gonna look at the way the atoms are bonded and I see that Oxygen is pulling with both hands; it's a double bond; it's gonna pull a lot of electron density towards it really creating a dipole.

So, you have a delta negative on the Oxygen and delta positive on the electron source, right. So, I am going to just take the electron source right now as water. Now, water when it attacks this particular acetone molecule, where will it really attack? It has to attack at that electrons sink right and as water is attacking that electron sink; remember as this Oxygen is forming a bond with this Carbon; it has to break one of the bonds because Carbon cannot form more than 4 bonds.

So, it breaks the pi bond and puts the electrons on that Oxygen. So, this is something we have seen, okay. So, the fourth rule which really talks about bond breaking will occur to avoid overfilling; it's nothing, but the octet rule; okay. So, in Organic Chemistry pretty much all arrows can be classified according to one of the three of the overall situations we have already seen.

One is the redistribution of pi bonds or lone pairs, second is the formation of a new sigma bond from a lone pair or a pi bond or the third is breaking of sigma bond to give a lone pair or a pi bond; okay. So, when we are learning new mechanisms first focus on the overall transformation okay. First always see what are the reactants; what are the products we are forming, okay? It might be a reaction in which atoms or groups are added or atoms or groups are removed.

So, when we add items to a particular reaction we call it as an Addition reaction. A reaction in which we remove atoms or different group of atoms, we call it as an Elimination reaction. And, when we substitute or when we really replace a group of atoms we call it is a Substitution reaction, okay or when we rearrange different atoms you call it as a Rearrangement reaction. But, really all of these types of reactions will really follow the same kind of arrow pushing. The arrows will always start from the electron and will go towards the electron sink or will go towards a positive charge.

So, understanding as oppose to memorizing a mechanism is really critical to mastering Organic Chemistry. In fact, almost all the Organic Chemistry mechanisms that we will see, you will see a couple of steps being repeated again, again and again and what your job is to do is to really identify the steps. So, like a proton donation or a proton removal or a nucleophillic attack, are the kind of steps that you will see happening again and again in most of the organic chemistry reactions that we will see.

And what our job is to identify these individual mechanism elements and then really understand how to assemble them into the vast mechanism, the overall mechanism that has many number of steps to really form a correct mechanism.