Mechanisms in Organic Chemistry

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Lecture-01
Introduction to Reaction Mechanisms

So welcome to this course on mechanisms in organic reactions. I would be your instructor for this course. My name is Professor Nandita Madhavan. I am from IIT Bombay. You can find more about me on the course webpage and also on my department webpage . So my interest is in general in organic synthesis and in this course we would be looking at a large number of organic reactions.

So when you think of organic reactions typically these are reactions involving chemistry of carbon compounds. So if I give you a very simple reaction, any organic reaction.

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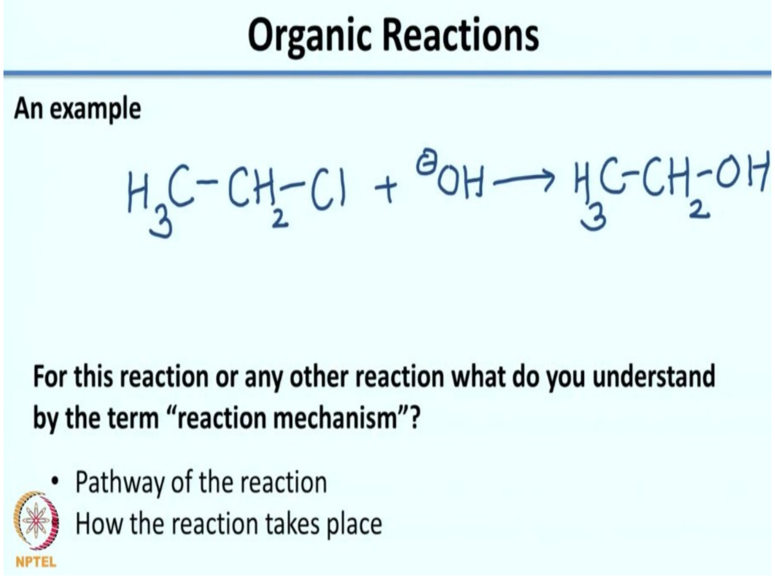

Organic Reactions

An example

$$H_3C-CH_2-Cl + {}^{\ominus}OH \longrightarrow H_3C-CH_2-OH$$

For this reaction or any other reaction what do you understand by the term "reaction mechanism"?

- Pathway of the reaction
  How the reaction takes place

So what you would see is, this is a very simple substitution reaction and you might have seen this in your 12th standard textbooks. So if I have, say, an alkyl chloride and I react it with a hydroxide ion, I end up getting an alcohol. Correct? So you might have seen this in your 12th standard textbooks. So now what I want to ask you is for this particular reaction or for that matter any other reaction that you have seen what do you understand by the term reaction mechanism?

So what I would like you to do is you can pause the video for a bit, take out a sheet of paper and write something which comes in your mind when you think of the term reaction mechanism. So you can go ahead and do that exercise. So when I do the same exercise in my classes some of the responses that I get are - a reaction mechanism is something which describes the pathway of a reaction, it also tells you how the reaction takes place.

Now to give you a little bit more detail into definitions, one can define a reaction mechanism as actual changes undergone by reacting molecules to reach the product state or sometimes people talk about chemical steps necessary for one molecule to be transformed to another.

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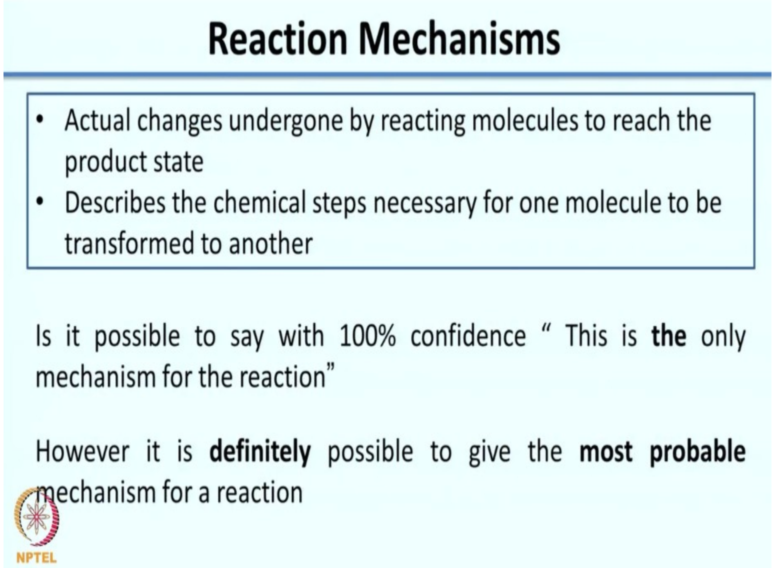

Reaction Mechanisms

- Actual changes undergone by reacting molecules to reach the product state
- Describes the chemical steps necessary for one molecule to be transformed to another

Is it possible to say with 100% confidence " This is **the** only mechanism for the reaction"

However it is **definitely** possible to give the **most probable** mechanism for a reaction

So essentially if you're thinking of going from say destination A to destination B, you can even think of traveling by road to one destination to another, reaction mechanism essentially is something similar where your two destinations are your reactant and your product and the road essentially is your reaction mechanism. Now having said this, I want you to think about one more question.

Now that I know a reaction is it possible for me to say with 100% confidence that this is the only mechanism for that reaction? So this is another question where I want you to think about it for like 30 seconds. Now, what you would see is one can propose what you would call a most probable mechanism but it is not definitely possible to say with 100% confidence that this is the only mechanism for the reaction.

Again, just like I told you for the earlier example of going from destination A to B, you can take one road to reach from A to B, but that might not be the only road. You might have different roads which take you from A to B. So you can say with 100% confidence that this might be the fastest road to reach from A to B but what you cannot say with 100% confidence is this is the only road to reach from A to B.

So now what we will be doing in this course is, we would figure out ways for you to propose a reasonable mechanism for a given organic reaction and how you would check whether this mechanism works by designing experiments. Now again if I give you the example of going from destination A to destination B. Suppose there are 2 of you, you and your friend and you have this discussion-you say that to reach from destination A to B the quickest way is to take a bus especially if you want to reach at 5:00 p.m.

So now let us assume your friend says no, no, no, the quickest way to reach from destination A to B is a train, again at 5:00 p.m. because as you know traffic conditions vary. Now how will you both check who is correct? The best way to do that would be at 5:00 p.m. one of you goes by the bus and the other person goes by the train. The same thing with the reaction mechanism. So if you want to check whether the mechanism you are proposing is correct, what you would need to do is design experiments which tell you which would be a reasonable mechanism.

Now once you do the experiment, what would you check? Does this match the hypothesis? So in the example I had given earlier you would check who would reach faster, you or your friend who took the bus or the train. Now if you find that your hypothesis matches the experiment then you can say this is the most probable mechanism.

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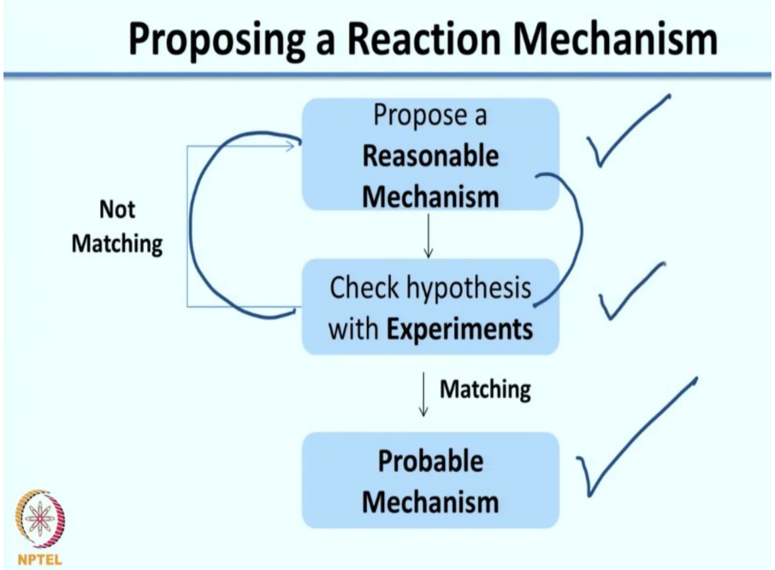

Proposing a Reaction Mechanism

Propose a **Reasonable Mechanism**

Check hypothesis with **Experiments**

Probable Mechanism

So in your case whoever reaches faster their hypothesis was correct alright? Now if it does not match what you would do is you would again go back, propose a new reaction mechanism and again check the hypothesis with experiments. So that is how this goes. So this is a continuous cycle. You start with a reaction mechanism, you check the hypothesis, if it works, great, if it does not work you keep repeating the cycle until you get a good mechanism.

Now for this to work in the first place you need to be sure that you are able to, a) propose a reasonable mechanism and b) design experiments to figure out if this mechanism is correct.

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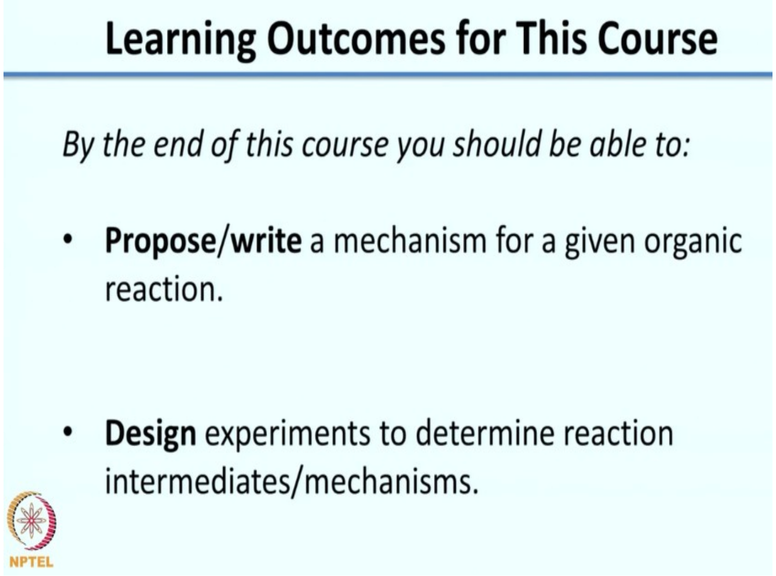

Learning Outcomes for This Course

By the end of this course you should be able to:

- **Propose/write** a mechanism for a given organic reaction.
- **Design** experiments to determine reaction intermediates/mechanisms.

So the learning outcomes for this course is, by the end of this course you should be able to propose or write a mechanism for a given organic reaction. So we would be giving you tools to help you write a reasonable mechanism for a given organic reaction and the other thing is you should be able to design at least some basic experiments to determine whether your reaction mechanism is correct or not.

So with this let us chart into what we were telling earlier, how you would be able to propose a reasonable mechanism and check the hypothesis with the experiment. So the first part is proposing a reasonable mechanism.

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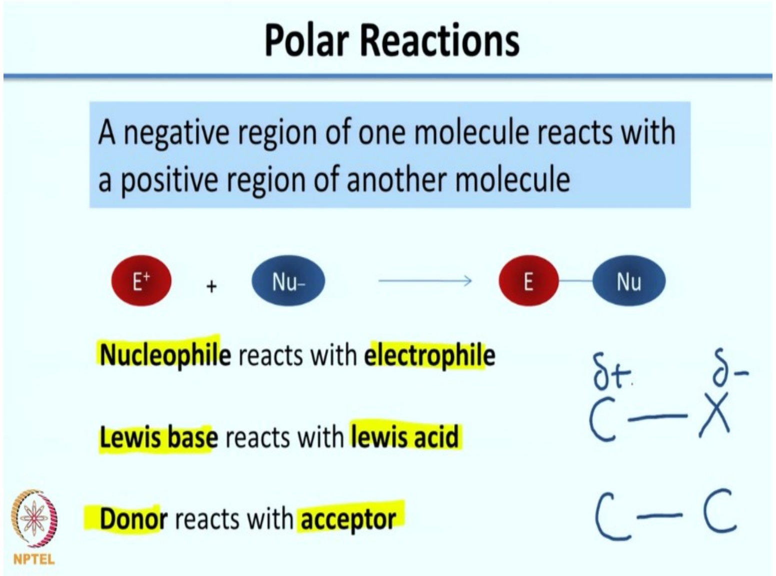

Polar Reactions

A negative region of one molecule reacts with a positive region of another molecule

Nucleophile reacts with **electrophile**

Lewis base reacts with **lewis acid**

Donor reacts with **acceptor**

$\overset{\delta+}{C}—\overset{\delta-}{X}$

C—C

So now if I were to broadly classify organic reactions, so what you see here on this slide is that I have used a very very basic classification of reactions. It is not overly complicated and you will also not see many structures here. So one type of mechanism is a polar mechanism. So now in a polar mechanism just like the name suggests, you have two intermediates which are charged so one would be positively charged and the other would be negatively charged and they would come together to give your product.

The second one is a radical mechanism. So now in the radical mechanism you do not have charged intermediates, what you have is radicals which would come together to give you your product and the third one which is concerted reactions, in these reactions all the bonding changes occur at the same time. So essentially there are no intermediates involved in these reactions. So what we will be doing is we would be looking at each of these mechanisms a little bit in detail. So that you have a general picture of how these reactions work.

So coming to the first one which is a polar reaction so polar reaction is one where a negative region of one molecule reacts with a positive region of another molecule. So essentially you have charged intermediates. you can have a positively charged intermediate reacting with the negatively charged intermediates. So many textbooks you will see terms like nucleophile, electrophile, Lewis base, Lewis acid, donor, acceptor.

Essentially, what all that means is you have some electron rich species and some electron deficient species. So since we are talking about organic reactions which essentially involve carbon, if I were to look at carbon and another species now if X right, now if X is carbon so if you are thinking of C-C what you see is both of these atoms would take the electrons of the bond in a similar fashion to each other.

So now if you have two atoms- C, X where X has a greater tendency to pull electrons to itself, now what will happen is X will end up having a small electron density over itself and carbon will have less electron density with itself. So even with a neutral molecule what you end up generating is a small positive charge and a small negative charge. Alright? Which is very essential for polar reactions.

So what we need to look at is what are ways in which there is this kind of a charge buildup in organic molecules.

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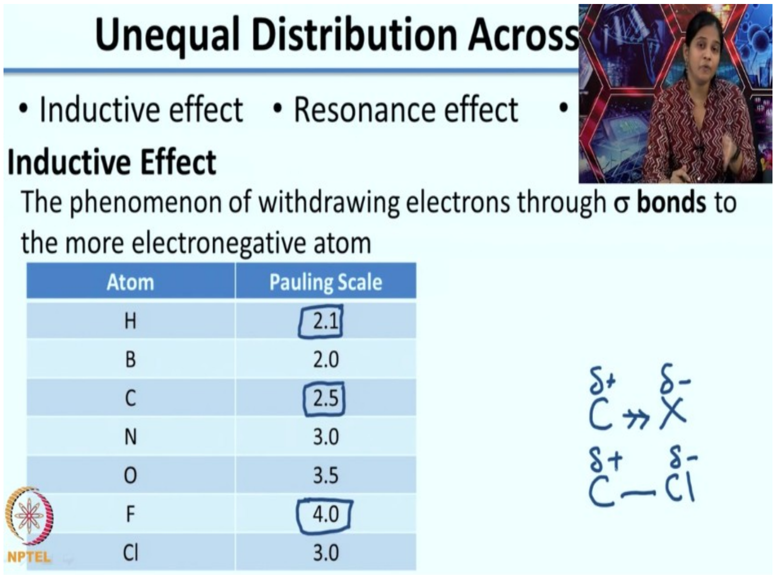

Unequal Distribution Across

- Inductive effect
- Resonance effect
-

Inductive Effect

The phenomenon of withdrawing electrons through σ **bonds** to the more electronegative atom

Atom	Pauling Scale
H	$\boxed{2.1}$
B	2.0
C	$\boxed{2.5}$
N	3.0
O	3.5
F	$\boxed{4.0}$
Cl	3.0

$\overset{\delta+}{C} \twoheadrightarrow \overset{\delta-}{X}$

$\overset{\delta+}{C} - \overset{\delta-}{Cl}$

So there are three effects which you would have come across even in your 12th standard books, they are inductive effect, resonance effect and hyperconjugation. So when you talk about inductive effect it is essentially the phenomenon of withdrawing electrons through sigma bonds and here comes a very important concept of electronegativity. So I had shown you in the previous slide where you can have essentially, so you can have this right? so now if X is an electronegative atom, what electronegative means is that X has a greater tendency to pull electrons towards itself from this bond that I have drawn here.

Now as it pulls electrons what you end up getting is you end up getting a δ- or a small negative charge and a δ+ which is a small positive charge on the carbon. Alright? so it is essentially imagine if you have two friends standing next to each other and you have a bag of chocolates the stronger one would end up pulling it pulling more of the chocolates towards themselves.

So similarly here, instead of chocolates we are talking about electrons. So if X is more electronegative it will tend to grab more electrons towards itself and as you know electrons are negatively charged hence you get a δ-, now so that you can compare like two friends I said one is stronger to compare which is more electronegative there is a scale called as Pauling scale and what Pauling scale does is it ranks atoms based on their electronegativity.

So shown here is I have just shown you a few atoms you can look at it in any textbook you would get the Pauling scale for all atoms and as the number goes up the electronegativity increases. So as you must have studied in your 12th the most electronegative atom here is your fluorine. So it has the greatest electronegativity value of 4 on the Pauling scale. Now related to fluorine if I were to compare, carbon has a lower electronegativity of 2.5. Correct?

Now hydrogen has now a lower electronegativity of 2.1, so if you imagine a bond which has a carbon attached to a fluorine or a chloride for that matter what would happen is because this is more electronegative you would see essentially a situation like this where you have δ- on Cl and δ+ on carbon. Now it is not important for you to actually remember all these numbers but what is very important for you just like the two friends I told you about you need to remember which is more electronegative. So what is more important is understanding the relative electronegativity and this is something which you must have studied in 12th along the periodic table as you go down the row the electronegativity increases which is why fluorine is the most electronegative atom there. So as you go there electronegativity increases.

Similarly as you go down, the group electronegativity decreases which is why chlorine is less electronegative as compared to fluorine. So one thing you need to remember is when you talk about inductive effect it is only the pulling of electrons through sigma bond, so it has to be through a bond. Alright? Not in space. Now having this concept in mind let us try to do a sort of game or an exercise together and I will help you out with this.

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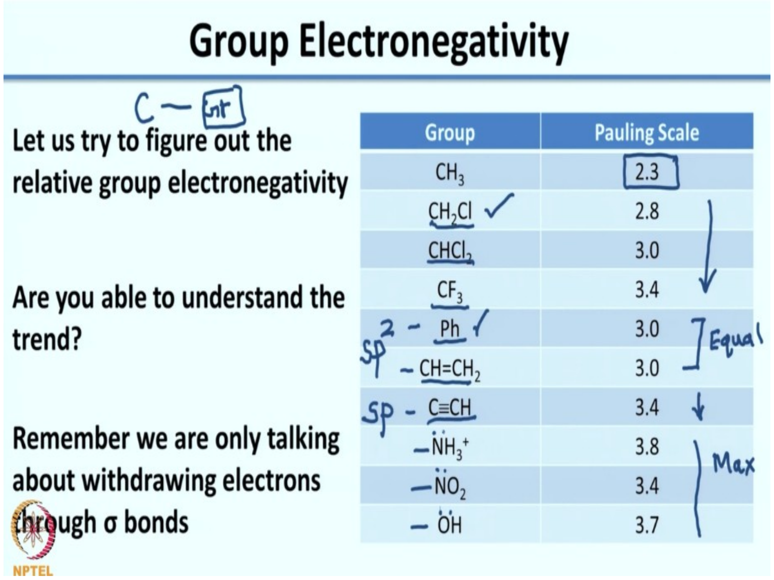

Group Electronegativity

Let us try to figure out the relative group electronegativity

Are you able to understand the trend?

Remember we are only talking about withdrawing electrons through σ bonds

Group	Pauling Scale
CH_3	2.3
CH_2Cl	2.8
$CHCl_2$	3.0
CF_3	3.4
Ph	3.0
$-CH=CH_2$	3.0
$C\equiv CH$	3.4
$-NH_3^+$	3.8
$-NO_2$	3.4
$-OH$	3.7

Now I have shown you a table here and this concept is called as group electronegativity. So instead of one atom what we think is suppose we have again I will try to draw it out to you so that it makes sense to you. Suppose we have carbon, alright? And we have this group attached to it whatever I have shown you here alright I am just calling it Gr for group, so as I change the group how does the electronegativity change.

And as I said relative values are very important so I have given you the value for methyl. So for methyl the value is 2.3. So now what I want you to do is as you can see I have given you a list of groups on this table, you can press the pause button on your video and take out a sheet of paper and then try to figure out as you see in these groups, for example here I have CH_2 Cl, $CHCl_2$ and CF_3.Alright?

Let us first look at these 3 and then I want you to figure out how the relative electronegativity would be and I will give you some time to work this out or you can take your own time by just pressing the pause button on your video. So now let us see if your answer matches with what we have here. You need not have the correct answer exactly. So what I want you to understand is as I go down here what is happening is that the electronegativity is increasing, right?

And I want you to now think about if for those of you who did not get the correct answer for this, I want you to again look at this trend and try to again think why could this be a trend. Now to give you a hint as I am increasing, as I am going down this table the number of halogen atoms increasing, so here I have 1 Cl, here I have 2 Cls and here I have 3 fluorines. Alright? So this is a hint I am giving to you.

Now let us look at the next group. The next group has phenyl, right? An alkene and an alkyne. All of these are now attached to the carbon and we are trying to figure out the relative electronegativity of these groups. Again you can press the pause button and try to work this out. So let us check our answers. So what you would see is compared to methyl and even to the alkyl chlorides what you see is, if you compare CH_2Cl with the phenyl what you see is, the phenyl is more electronegative and what you would see is both of these are almost equal. Whereas, if I have a $C=C$ the electronegativity again increases. Alright? So these two are almost equal and what you would notice now is in the last set where I have NH_3^+, NO_2 and OH, so this is the last set what you would see is here you have the maximum electronegativity values. Now why is this so? So what I would like you to do is look carefully at these trends and try to understand it yourself before I explain it to you because that would be more effective for you. Alright?

So what I would like you to do is I would like you to see and understand the trends that are given here. Alright? And the hint I am trying to give you is that remember we are only talking about withdrawing electrons through sigma bonds. Alright? So now to understand these trends, now that you have had some time to think about it what you see is when you go to phenyl and the alkene, both of these are sp^2 hybridized.

So these are both sp^2 hybridized as you see the percent s character increases that means the nucleus has a greater tendency to grab the electrons because the percent s character has increased which is why it is more electronegative. Remember the stronger friend? So in this case the nucleus percentage is increasing, the s, I am sorry, the s character is increasing in the nucleus so it can grab electrons.

So the biggest effect you can see is now when I have an sp hybridization, the electronegativity goes up. Now in all these cases where I have NH_3, NO_2, OH a common mistake which students do and I see this even in my classroom is that they confuse this with another effect where the lone pairs actually play a role. But in this case as I told you again we are only talking about the effect through the sigma bond.

So here what you would only look at is the electronegativity difference. So nitrogen and oxygen are more electronegative than carbon which is why they have a greater value of electronegativity of 3.8 and 3.4. Of course in this case the value is very high because you are talking about a charged species.

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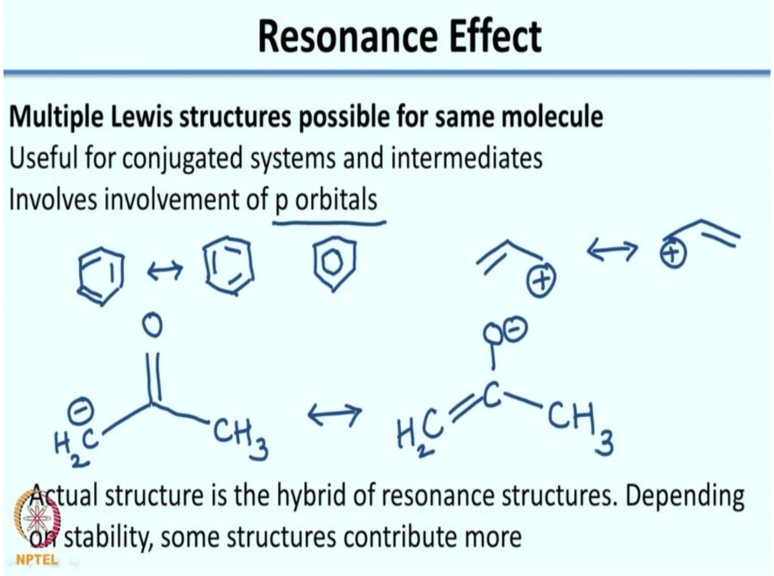

Resonance Effect

Multiple Lewis structures possible for same molecule

Useful for conjugated systems and intermediates

Involves involvement of p orbitals

Actual structure is the hybrid of resonance structures. Depending on stability, some structures contribute more

So now that we have some idea of the inductive effect, another effect, now in this effect, the lone pairs play a very important role. This effect is called as resonance effect. So resonance effect is where you have multiple Lewis structures for the same compound and you must have seen this again in your books, so what you must have seen would be benzene, so if you have benzene you would have seen an arrow like this shown to depict resonance and these would be the two resonance structures of benzene and the actual structure is actually shown as the hybrid of both the resonance structures. So the actual structure is the hybrid of both the resonance structures and in some books the actual structure is shown as a circle to show that all these electrons are moving along. These are very useful for conjugated systems. So conjugated systems mean systems for example where I have say a positive charge here.

So a resonance structure for this would be, also it involves p orbitals so a lot of times what you would see is you would have structures, so this is the structure of an intermediate, a resonance structure of that would be, now do you actually need to memorize all these structures to be able to write multiple Lewis structures? No. These are very logical and you just need to remember how to show movement of electrons. Right?

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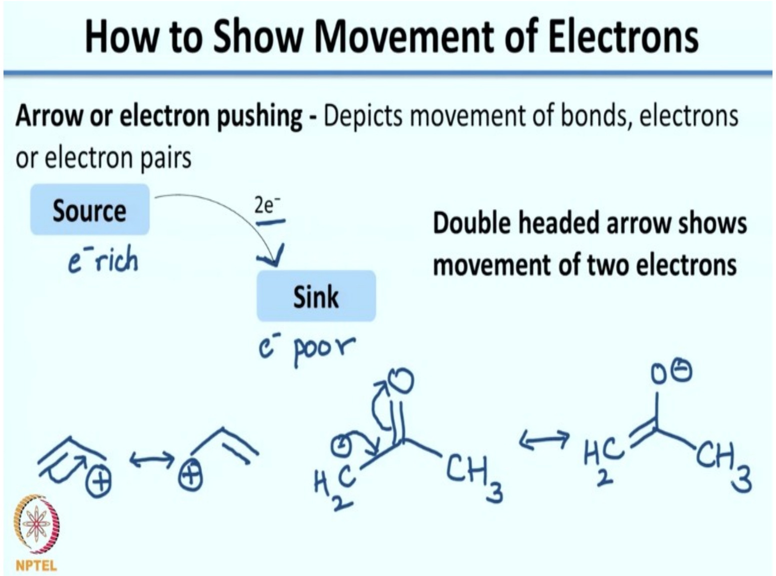

How to Show Movement of Electrons

Arrow or electron pushing - Depicts movement of bonds, electrons or electron pairs

Source

Sink

Double headed arrow shows movement of two electrons

So one way or the convention to show movement of electrons is what is called as arrow or electron pushing. This depicts movements of electrons or electron pairs. So how do you show the movement of electrons? This is very useful in writing multiple Lewis structures in a very systematic way. So the arrow pushing or electron pushing depicts movement of electrons in a way such that you go from an electron rich species which is your source, and to the sink which is electron poor right.

Just like it suggests source means it has lot of electrons, sink means it is very poor and you show it by a double-headed arrow, so double-headed arrow indicates you have two electrons moving. So now if I were to look at the structures that I showed you before, if I have, so here it is very clear what your source is, it is these pi electrons. So you start by drawing an arrow from the source to your sink.

So now that these electrons move this carbon becomes electron deficient, so what you end up getting is you end up forming a new double bond and a positive charge here. Make sure you draw the direction as I have shown you here, otherwise it would be incorrect. You can also think of the earlier structure which I showed you CH^{2-}, so here this would be your source, so the source will come here.

Now carbon cannot have so many electrons so it will push the electrons onto oxygen. So your resonance structure would be alright? So you can try practicing this arrow pushing, picking up any examples from textbooks where they show you multiple resonance structures.

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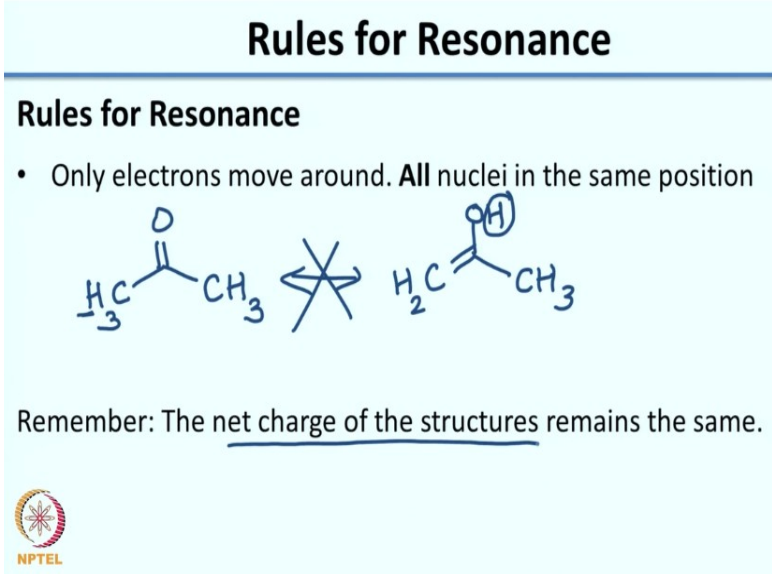

Rules for Resonance

Rules for Resonance

- Only electrons move around. **All** nuclei in the same position

Remember: The net charge of the structures remains the same.

Just remember that there are some rules that you need to remember; only electrons move around when you look at the Lewis structures. The nuclei have to be in the same position, so similar to the example that I had given you earlier, suppose I take and then I write another structure, now what has happened is the hydrogen has moved here, so these two are not resonant structures. So be very careful when you write resonant structures. Also remember that the net charge of the structures remains same. Right?

So in the previous example what we had seen is the only difference was that a negative charge had moved from a carbon to an oxygen, but the net charge will remain same which is logical because only electrons are moving. So if you write a resonance structure for a neutral molecule if you have a resonance structure which shows some sort of charge then you know that you have made some mistake in drawing the Lewis structure.

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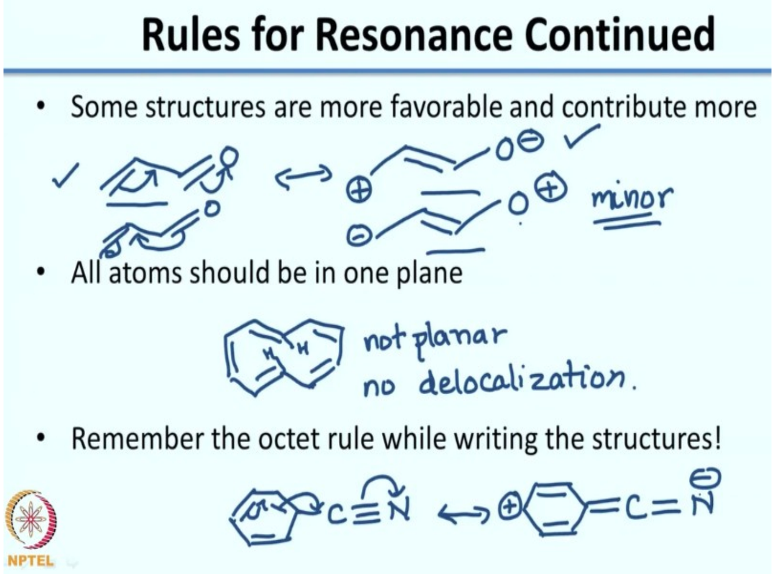

Rules for Resonance Continued

- Some structures are more favorable and contribute more
- All atoms should be in one plane
- Remember the octet rule while writing the structures!

The other thing you need to remember is some structures are more favorable and contribute more. For example if I have so now I can write resonance structures where alright, I can also write a resonance structure where I have that would be if I were to push electrons where I am pushing in the reverse direction. Now out of these 3 structures, so I have structure 1, structure 2, structure 3.

This would be the most stable because they result much charge separation. Now between these 2 this structure would be more favorable because you have a negative charge on an electronegative atom, whereas here you have a positive charge on an electronegative atom. So it will be a very minor contributor. Alright? The other thing is resonance involves delocalization or sharing of electrons.

As you see in all these cases it is either pi bonds or lone pair of electrons which move. So all the atoms must be in one plane and this is an example which you would have seen in your textbooks where if you have a molecule like this because of sterics this molecule is not planar, so no delocalization. Alright? And of course whenever you write all these structures you have to ensure that you remember the octet rule.

For example if I were to write the structure so if I were to write the resonance structure of this one plausible resonance structure could be again because we are moving from this center, I generate a positive charge here. Now I cannot push any more electrons on to nitrogen because I would be violating the octet rule. Alright? So these are the rules for resonance and as I said some structures contribute more than the other.

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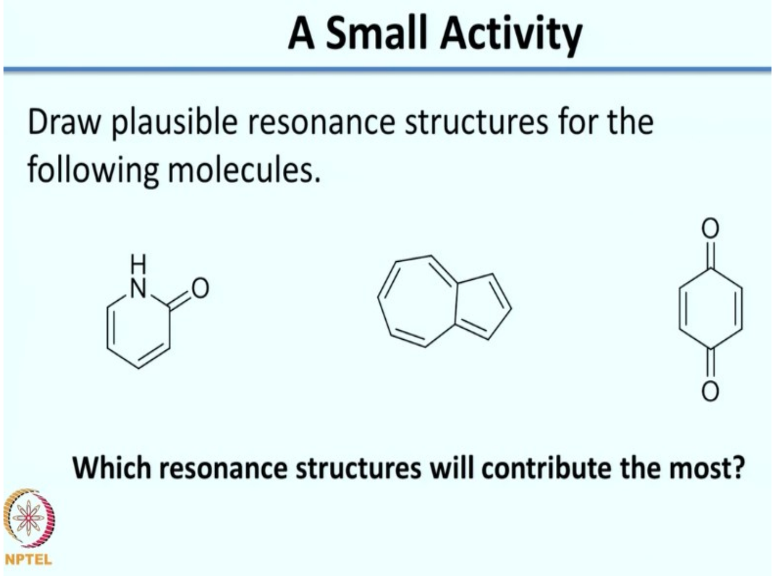

A Small Activity

Draw plausible resonance structures for the following molecules.

Which resonance structures will contribute the most?

So before we stop this lecture what I would like you to do is, I would like you to do this as a mini homework where you try to draw plausible resonance structures for the three molecules that you see on the screen and what you should figure out is which resonance structure will contribute more for each of these molecules. So remember the rules of resonance which I showed you in the earlier slide and use the concept of arrow pushing to clearly show each of the resonance structures.

If you have any doubts you can take this up in the discussion forum, but initially I would like each of you to spend the effort yourself in trying to write all possible resonance structures for the following molecules and find out which resonance structures will contribute more. So thank you and we will see you in the next lecture where we will look at answers to this problem.