Mechanisms in Organic Chemistry
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Lecture-35
General Catalysis: Part A

Hello and welcome to the last week of this course- Reaction Mechanisms. So just a recap as usual of what we did in the previous class. So in the previous class we were looking at catalysis. Specifically, we were looking at bronsted acid-base catalysis.

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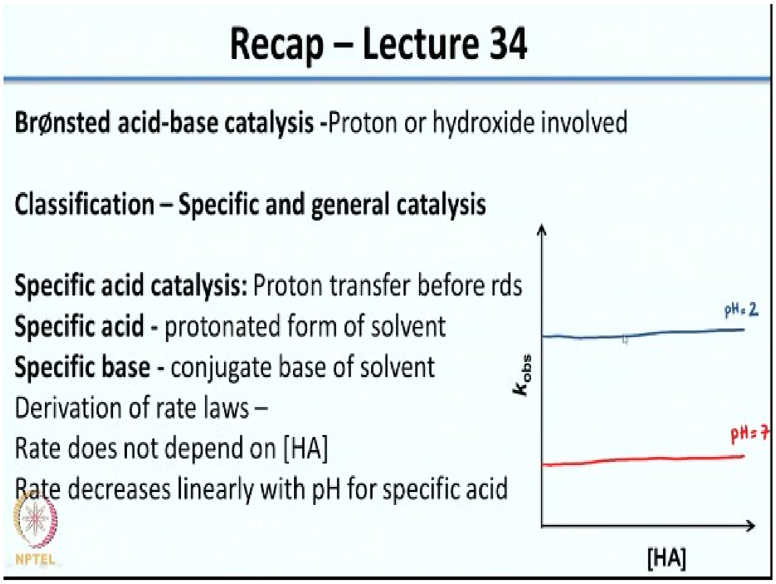

Recap – Lecture 34

Brønsted acid-base catalysis -Proton or hydroxide involved

Classification – Specific and general catalysis

Specific acid catalysis: Proton transfer before rds
Specific acid - protonated form of solvent
Specific base - conjugate base of solvent
Derivation of rate laws –
Rate does not depend on [HA]
Rate decreases linearly with pH for specific acid

So this involves some sort of proton or hydroxide transfer. Now further we had classified it as specific and general catalysis and we had mainly looked at specific acid catalysis. So in specific acid catalysis, the main thing you need to remember is that proton transfer occurs before the rate determining step. So, in other words Proton transfer is pretty fast and is not the rate determining step.

It happens before the rate determining step and then why is it called specific acid of specific base? The reason being that you can put whichever acid you want in the solvent but what catalysis it or the kinetic essentially depends on the protonated form of the solvent for specific acid and the conjugate base of solvent for specific base. So if you are talking about water, then essentially, the reaction kinetics will depend on only concentration of H_3O^+.

It will not depend on concentration of HA which is the other acid that you might be adding. Similarly if you are looking at specific base the kinetics will only depend on concentration of OH^- if you are talking about water as solvent and not any other base that you would have added to the reaction mixture and we had looked at derivation of rate laws and essentially when we derived the rate laws what we saw that was that the k value depended on only the concentration of H_3O^+ or OH^-.

So it did not depend on concentration of the acid which is HA and if you plot the k_{observed} versus concentration of HA essentially you will get a straight line and shown here are 2 straight lines at 2 different pHs. In the case of specific acid, you will have a higher k_{observed} at the lower pH as compared to the higher pH. So if you were to plot the log of k versus pH, what you would see is, you would see a linear decrease in the case of a specific acid. So as the pH will increase the k value will decrease for specific acid.

So now let us move on to the general acid and general base catalysis. Now in general acid catalysis what you must remember is that the proton transfer occurs in the rate determining step. Not before. In the rate determining step. So that is what is general acid catalysis.

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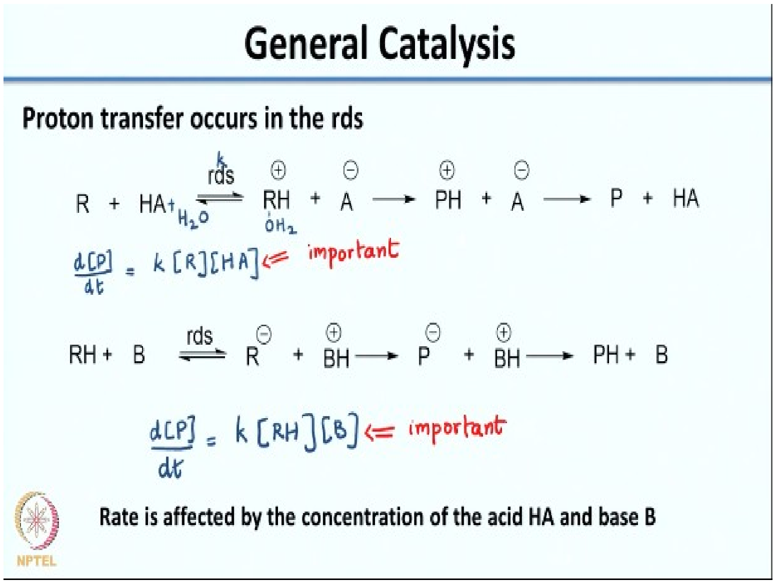

General Catalysis

Proton transfer occurs in the rds

$$R + HA + \underset{H_2O}{} \xrightleftharpoons{\overset{k}{\text{rds}}} \underset{OH_2}{\overset{\oplus}{RH}} + \overset{\ominus}{A} \longrightarrow \overset{\oplus}{PH} + \overset{\ominus}{A} \longrightarrow P + HA$$

$$\frac{d[P]}{dt} = k[R][HA] \Leftarrow \text{important}$$

$$RH + B \xrightleftharpoons{\text{rds}} \overset{\ominus}{R} + \overset{\oplus}{BH} \longrightarrow \overset{\ominus}{P} + \overset{\oplus}{BH} \longrightarrow PH + B$$

$$\frac{d[P]}{dt} = k[RH][B] \Leftarrow \text{important}$$

Rate is affected by the concentration of the acid HA and base B

So shown here is a very simplified version of the general acid catalysis equation. So you will have R + HA which is the rate determining step to give you RH^+ + A^- which will then give you PH^+ and followed by P and then HA is generated. For simplicity I have not shown water here but in reality what you will also have is, you will also have water and a lot of times what you have is a complex of, so the whole thing would be charged depending on whether it loses the proton or not. So you have a species like this that would be generated

where you have the water also playing a role. When we look at specific examples later it would make more sense to you. So now if you were to derive the rate law for this which is the rate determining step? The first step is the rate determining step. So if I were to write which is essentially the rate it would be given by k let us say k is the rate constant for this and if water plays a role, concentration of water will also come in. But as you know most of the times we do not take that into consideration.

So now what you see is, when you are looking at the rate the concentration of HA is actually playing an important role. So essentially what you see is concentration of HA is important and it cannot be neglected. Whereas what you shown specific acid catalysis was that it mainly depended on the concentration of H_3O^+. Similarly, you can derive the expression of the general base catalysis. Again I have simplified this and not included water here.

So here again if I were to write the rate, the rate would be given by, so here again what do you observe? You see that concentration of B is actually important. Essentially when you do the kinetics for these reactions which are under general acid or general base catalysis, what you would see is that the concentration of the acid or concentration of the base plays a very very important role. So that is what I have written here- the rate is affected by concentration of the acid HA and base P. So the main difference here with specific acid catalysis was that,

in this case, the acid that you add is involved in the rate determining step. So that is the big difference between specific and general catalysis. Now what if you have a reaction in which the acid that you are using is actually water and you have protonation in the rate determining step? So in this case what will your HA be? If you are using water your HA would be H_3O^+. So in this case although the protonated solvent is what is important, but it is involved in the rate determining step so that is why it would be a general acid catalysis.

So do not get confused with this term specific and general. Just remember that specific means it is very very specific to protonated form of the solvent. General means it can be any acid whatever you add. If you want to add acetic acid then it would be catalysed by acetic acid and that concentration will be important. So now that you understood this concept, the difference between specific and general catalysis, let us see if you are able to plot this now.

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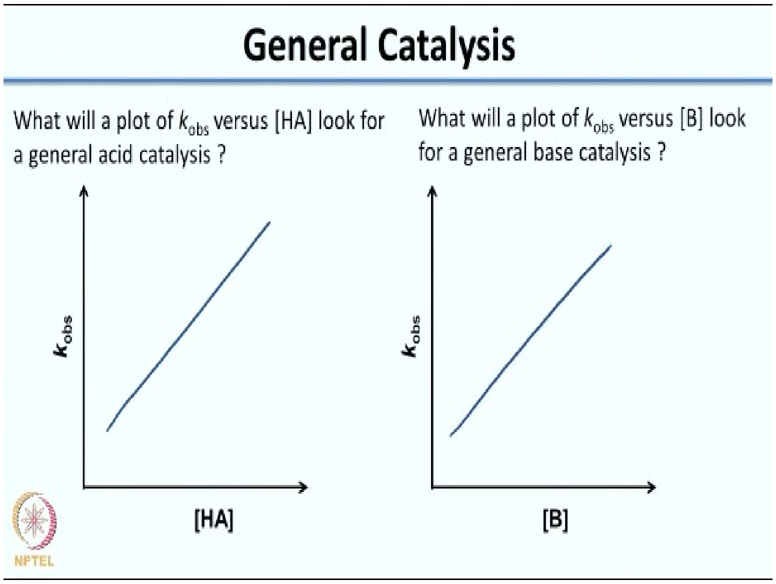

General Catalysis

What will a plot of k_{obs} versus [HA] look for a general acid catalysis ?

What will a plot of k_{obs} versus [B] look for a general base catalysis ?

So what would be a plot of k_{observed} versus concentration of HA for general acid catalysis? So I want you to think about this and you can press the pause button, look at the equation that we had written in the previous slide and then try to plot it. In the earlier case for specific acid it was a straight line, in this case which was parallel to the X-axis let us see what will it will be in this case. So you can press the pause button and try to write the answer in your notebook. Alright let us see if you were able to get the answer correctly. Now as the concentration of HA increases,

since now you have a direct dependence on concentration of HA, in the kinetics expression what you would get is you would get a straight line which would be increasing. Alright? Now what will the plot look like for general base catalysis? So now you are plotting k_{observed} with respect to concentration of B. So now I want you to think of what the graph will look like. Again, press the pause button and write it in your notebook.

So let us see if you got this correct. Even in this case there is a direct correlation correct? So here also it will not be any different. It will be a straight line. Alright? So, what you would see is the k_{observed} will obviously increase with the concentration of the base. In one case with the concentration of acid and the other case with the concentration of base.

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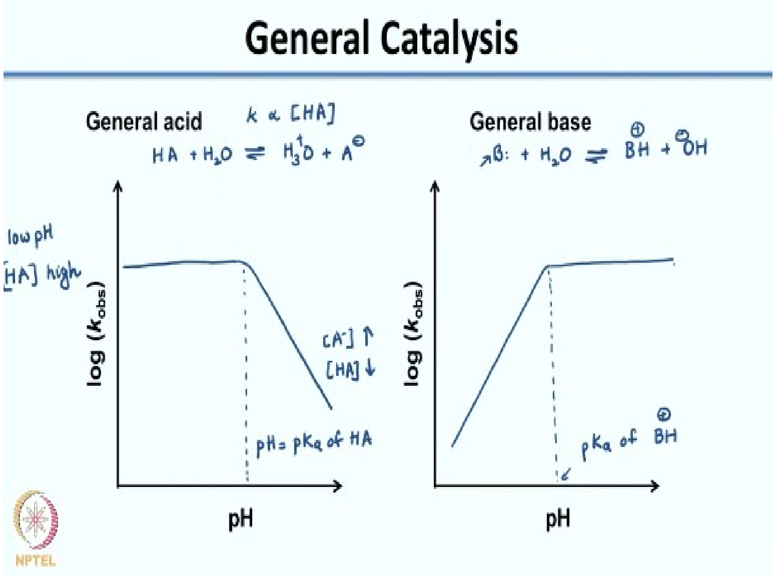

General Catalysis

Now like last time this is slightly more involved. I want you to think about how log of k_{observed} will vary with pH for general acid catalysis. So I want you to remember one thing. Remember that the k_{observed} depends on concentration of HA. Alright? So now what you need to think about is how the concentration of HA will change with pH. Alright? This is the hint I have given you. So you need to think about how when you change the pH the concentration of HA will change.

And if you need one more hint you can think of the Henderson Hasselbalch equation. So I will request you to press the pause button and try to draw this graph. So let us see what happens. At low pH, correct? So when you have the pH very low, it essentially indicates that HA would be in its own form which is the undissociated form. So what you would have is, you will have at low pH, a higher concentration of HA. Now you need to look at this equilibrium which is right? So at low pH you have a great concentration of H_3O^+. The equilibrium is towards the left.

Now what will happen as you increase the pH? When will there be a major change? The major change will be when you have HA dissociating. Right? So it has a dependence on the pKa of HA and if you remember your Henderson-Hasselbalch equation, right? When the pH is equal to pKa of the acid what do you have? You have an equal concentration of HA and A^- correct? So the graph will look something like this, where what you see is it would remain a straight line without much change because the concentration of HA would remain the same.

and then beyond the point what you see is you would see it starting to decrease with an increase in pH. So what is happening here? At this point the pH will be equal to the pKa of HA. So what will happen beyond this point would be that concentration of A^- is what will start increasing and concentration of HA will start decreasing. Alright? So beyond this point what you see will be that you will have lesser and lesser and lesser concentration of HA in the solution and we had just seen in the previous slide that the k_{observed} actually increases with the concentration of HA. So as the HA concentration is decreasing,

what would you see is that you would see a decrease in the rate that you observe. So now that you understood this concept, I want you to work out what the graph will look like in the case of a general base reaction. Alright? And as a hint what you can think of is when you look at a base, you can think of this equilibrium and remember the *k* in this case depends on concentration of B. alright? So that is what is important for the *k* value in this case. So now press the pause button and try to write what the graph will look like. Alright,

so let us see. In this case what happens is, at a very low pH you would have B exist mainly as BH^+. So B will exist mainly as BH^+ so what happens if you do not have concentration of B very high in your solution. So what you see would be that it will be, it will slowly slowly increase right? As you increase the pH and then there will be a point at which it will become unchanged. So that means BH^+ has completely dissociated to B at this point and again

what would this point correspond to? You can think a little more. This point would correspond to pKa of BH^+. Right? So when your pH is equal to the pKa of BH^+ it will start dissociating and then you have this rapid dissociation. Usually you see a sigmoidal curve if you remember from your titrations that you have always done. So what you would see is beyond that point you would have the concentration of B not changing much which is why you would see a straight line. Alright? So this is very different from what we had seen in the case of specific catalysis. So now let us try to look at examples.

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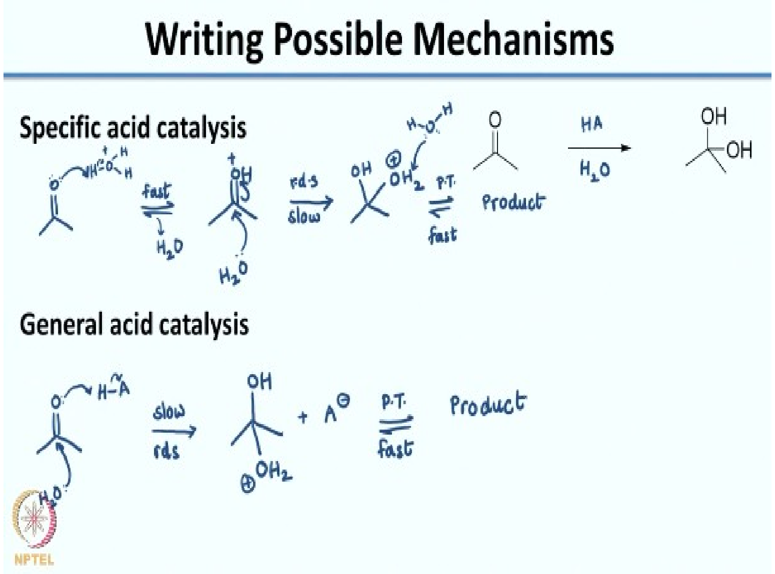

Writing Possible Mechanisms

Specific acid catalysis

General acid catalysis

Let us look at an example of this ketone right. This ketone is being hydrolyzed. Alright? So now when you get this product let us look at how you would write the mechanism had this taken place by specific acid catalysis. So we are looking at a hypothetical situation. Let us say this reaction was being catalyzed and the mechanism was such that it is similar to a specific acid catalysis. How will you write that mechanism?

I will show you in this case. So when you look at specific acid catalysis what is the thing you need to remember? Orotonated solvent is what is important. So let us say we doing this reaction with an acid HA in water. Alright? So H_3O^+ is what we are looking at. So now let us say that you have your ketone right? Remember in a specific acid catalysis the proton transfer occurs quickly before the rate determining step. So let us say the proton transfer is now occurring quickly from the protonated solvent

which is H_3O^+ this is O. So let us say and this will occur fast or slow? It will be fast because we are looking at specific acid catalysis. So now what you get would be and then water will leave.

So now that you have this species, you will have water add in. Do not forget your arrow pushing from the very first week. Alright? So when you have this add in, this process would be the rate determining step or the slow step and what you get would be right?

Now after this what would happen is, you would have a quick proton transfer. Again this would be fast. So this proton transfer would be again from water; will grab this proton to give you your product. Alright? So now what has happened? You have the proton transfer occurring quickly in the first step followed by the addition of water which is the rate determining step. Now let us assume this reaction takes place by a general acid catalysis. So now what do you need to remember?

The proton transfer is occurring in the rate determining step. So how will you write this? In this case so you have your acetone. Let us say now it is being catalyzed by the acid HA. Remember now concentration of HA as important. So let us say that this is getting protonated and as you know proton transfers are usually quick, so if the general acid catalysis, presumably the water is also adding in at that point; and this is your slow step or your rate determining step.

So then what you get would be; now once you have this, so this looks very similar to the intermediate we had seen above here; You have proton transfer, again, this would be fast to give you your product. Alright? So these mechanisms are written, so these are hypothetical possible mechanisms, that we have written to show how the reaction will take place had it gone by specific acid or general acid. So this just shows you how the mechanism would look in each of these cases. So now that I have shown it to you for specific acid and general acid catalysis I want you to write the mechanism

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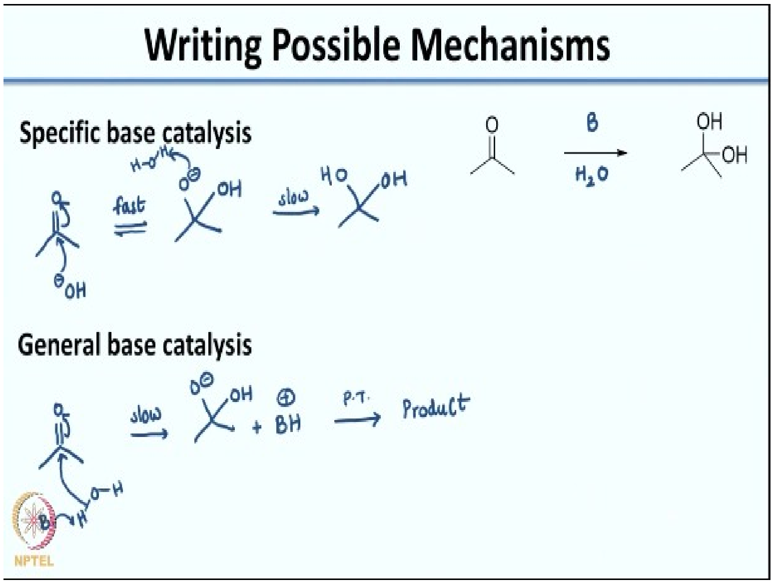

Writing Possible Mechanisms

Specific base catalysis

General base catalysis

for specific base and general base catalysis. So here you can assume that you are adding a base B and again the solvent is water. So go ahead and write the mechanism first for specific base catalysis. So in specific base catalysis let us see if you have this correctly. So I have my acetone right? And now what is the base that you have in your specific base? It is OH^-. So you have OH^- . OH^- will add in. so what will you get? This will be fast. Right?

So once you get this anion, this will abstract a proton. Remember there will be no H_3O^+ we are talking about a basic medium. So this will grab a proton from here. So then what you would get would be your product. So, this would be a slow process. Now what will happen in a general base catalysis? Now in a general base catalysis, the proton transfer is rate determining and concentration of base is important. So let us say you have base in your reaction medium which is water. So let us say the base grabs this proton.

So then you have this bond breaking and what you would get would be slower process where you have again O^-, OH plus BH^+. Alright? So now that you get this, the next step would be formation of the product. Again via another proton transfer. Alright? So this is how you would write possible mechanisms for specific base and general base.

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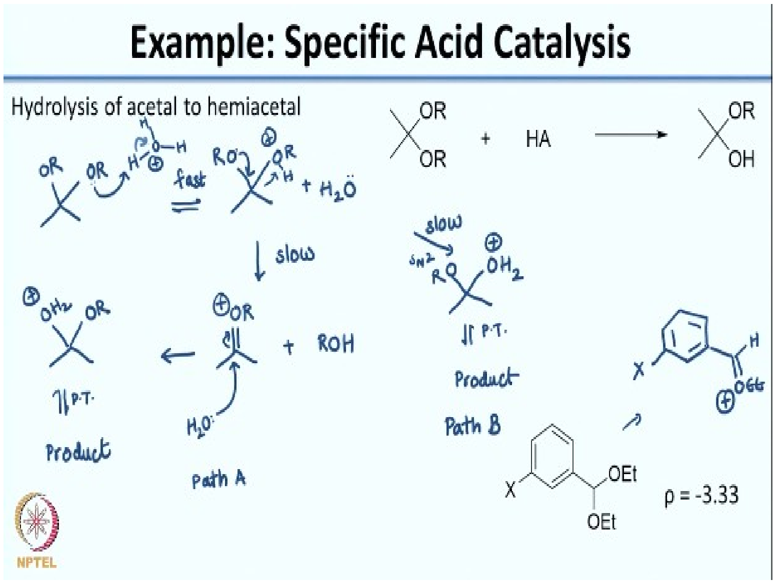

Example: Specific Acid Catalysis

Hydrolysis of acetal to hemiacetal

ρ = -3.33

Now let us look at specific examples. Okay? There are too many terms specific coming here. Now I mean the english word specific not specific acid. Let us look at hydrolysis of acetal to hemiacetal and let us look at this specific example of specific acid catalysis. So here you have the acetal being hydrolyzed to hemiacetal. Alright? So now I want you to write possible mechanisms for specific acid catalysis. We have just done that for acetone.

So I believe this would be easy for you to do. So go ahead and do that in your notebook. You can check your answers looking at my slide later. Alright. So let us write the mechanism. So you have OR, OR and again specific acid catalysis, we are looking at H_3O^+. Say you have this grabbing the proton. So what you get would be; so you get this product. Now there are 2 mechanisms that you can write once you get this product.

One mechanism is where you have this lone pair coming down to give you this is oxonium ion plus ROH. Then after that you will have water adding in to give you; and then you have a quick proton transfer to give you your hemiacetal product. Alright? Now because this is specific acid catalysis this step would be fast and then this step would be slow. The other option is you can think of, So this is pathway A.

The other option is, once you form the first intermediate, you can think of water attacking and it undergoing an S_N2 like mechanism to give you and of course this will undergo proton transfer to give you the product. So both of these mechanisms you can write for a specific acid catalysis. Now how do you know which of these mechanisms is operative? So what is found is, that for this particular acetal, so you have an aromatic unit right next to the acetal and X; so that means what was the experiment that was done?

It was a Hammett correlation. So the linear free energy relationship was determined for this particular reaction as in hydrolysis of this particular acetal and the rho value was found to be -3.33. So that means a large negative value. So whatever you studied before for the Hammett plots can you tell me which path is operative? Path A or path B? Again press the pause button. You can look at your notes from earlier and figure out the answer.

So the high negative value suggests that you have a positive charge close to the aromatic ring here. So that shows that it goes via path A. Right? because in path A you will generate an intermediate which would be, correct? So if you write the resonance structure of this you have the positive charge in conjugation with the aromatics ring. So that is why you see such a negative rho value. So here using the Hammett correlation, you could say that it goes via path A.

Now suppose the same reaction goes via general acid catalysis. How will you write the mechanism? So I want you to do that as homework and when we come back in the next lecture,

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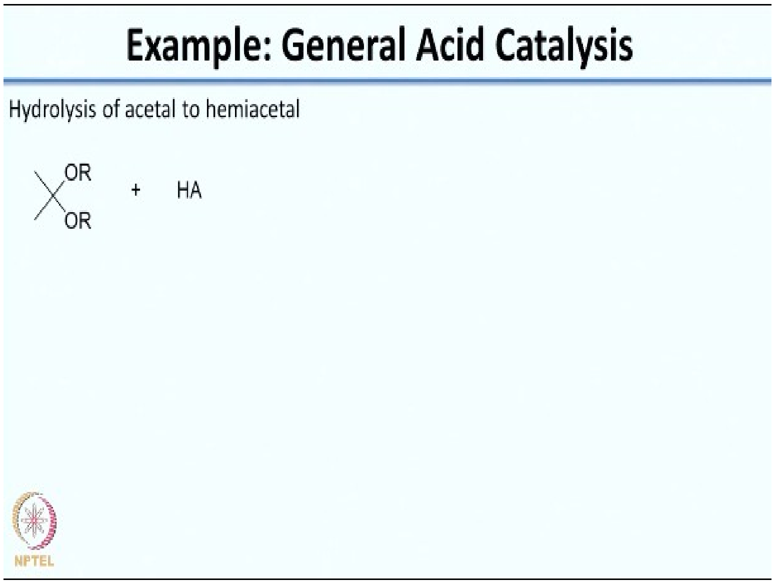

Example: General Acid Catalysis

Hydrolysis of acetal to hemiacetal

we will see how this reaction mechanism takes place and do you actually observe such a mechanism? Because usually one would assume that for the acetal hydrolysis it would have to go by a specific acid catalysis because you do not have a great leaving group. So you would need protonation to be the first step and it would be a quick step. So we will meet again in the next class. Before that try to work out this mechanism and we will see if you have it right in the next lecture. Thank you.