Rate Processes
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Module No. # 01
Lecture No. # 18
Acid Base Catalysis

Good morning everybody.

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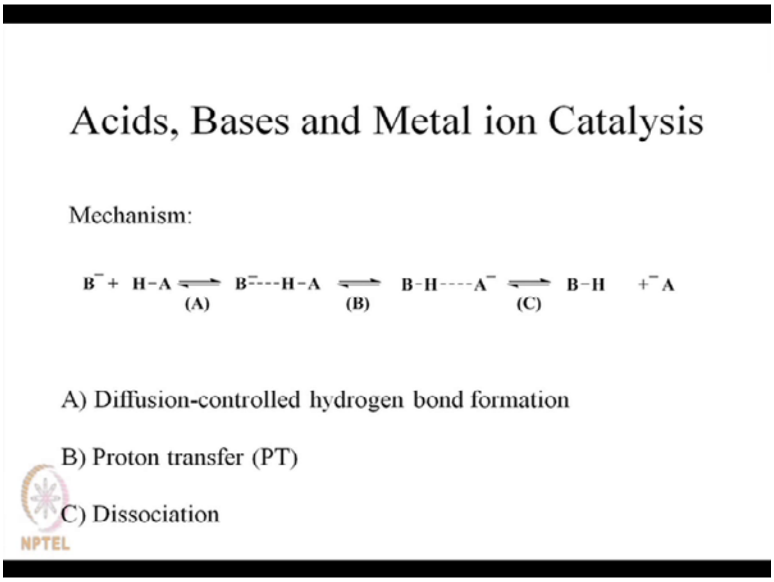

Acids, Bases and Metal ion Catalysis

Mechanism:

$$B^- + H\text{-}A \underset{(A)}{\rightleftharpoons} B^-\text{---}H\text{-}A \underset{(B)}{\rightleftharpoons} B\text{-}H\text{----}A^- \underset{(C)}{\rightleftharpoons} B\text{-}H \quad + {}^-A$$

A) Diffusion-controlled hydrogen bond formation

B) Proton transfer (PT)

C) Dissociation

Today we will continue with kinetic of some specific reaction and under this heading we will start with acids, bases and metal ion catalysis. So, the mechanism goes as like it is A - it is a general mechanism like this, that is B minus and this is your acid. Then, this is your acid means, H-A; it is an acid. So, this consists of 3 steps primarily that is, this is your substrate or maybe this is A base also which abstracts the proton from this acid and during abstractions means to do this abstraction, it should follow or it is you know postulated to follow such scheme.

Now, here what happens is that, there is a bond formation there is a bond formation which is you know hydrogen bond formation between this base and this acid and then, what happens is that this bond this H-A bond stretches and this hydrogen bond you know this length squeezes. And, as a result which basically this hydrogen is shifting its position from this region to this region. I mean, it is moving this way and ultimately there is A bond formation between B and H and this bond (( )) resulting in A minus and

B-H. Basically, since we started with B minus so B-H neutral has been formed. So, to (( )) acid base catalysis, we should know means, how this acids are acting. Now, acid means it is basically a proton; so, for this proton to act as a catalyst the following scheme may be useful. Now, basically a is diffusion controlled hydrogen bond formation; then, it is a proton transfer; this second step is the proton transfer and then the last step is your dissociation that is dissociation of original H-A bond. Now, diffusion controlled means this formation of this complex I mean, B H-A complex requires that this interacting substrates should come close to each other and since it is coming close to each other. It occurs by the process of diffusion inside the solvent. So, it swims close to you know this B minus, so 3 steps for this, such type of catalysis acid base catalysis. So, diffusion controlled hydrogen bond formation proton transfer that is PT and dissociation.

Now, faster proton transfer has been found to occur with this nitrogen oxygen or sulfur. So, this B minus, if the interacting group or integrating atom in B is having nitrogen oxygen or sulfur, that is the atom which interacts with this hydrogen to form a hydrogen bond.

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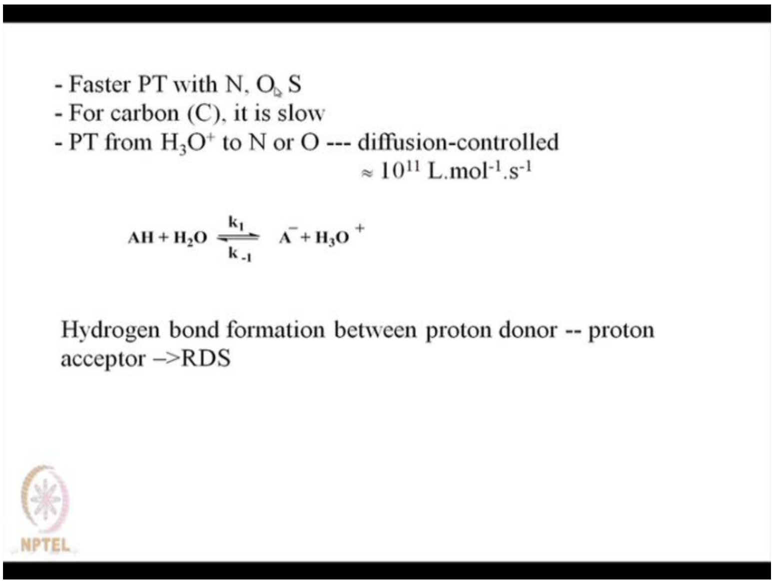

- Faster PT with N, O, S
- For carbon (C), it is slow
- PT from H_3O^+ to N or O --- diffusion-controlled

$\approx 10^{11}$ L.mol^{-1}.s^{-1}

$$AH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + H_3O^+$$

Hydrogen bond formation between proton donor -- proton acceptor –>RDS

If it is nitrogen, oxygen or sulfur then, this proton transfer has been found to be very fast if it is carbon then it is slow and proton transfer from hydronium ion H3O plus to nitrogen and oxygen. It is diffusion controlled; this is very fast. Basically, it depends on how means how fast these interacting substances are coming close to each other. So, and that is limited by the diffusion of them; diffusion that is how they are diffusing close to each other that is why it is called a diffusion controlled and the rate is 10 to the power 11 liter mole inverse. Very fast, so you see that AH it is an acid here H2 is the base forward reaction. The formation of A minus and H3O plus and back reaction is the back hydrogen or back proton transfer to give you AH. So, this is your acid; its corresponding ion, this is base corresponding H3O plus. So, hydrogen bond formation between proton donor and proton acceptor; so this one is proton donor and this one is proton acceptor is the rate determining step.

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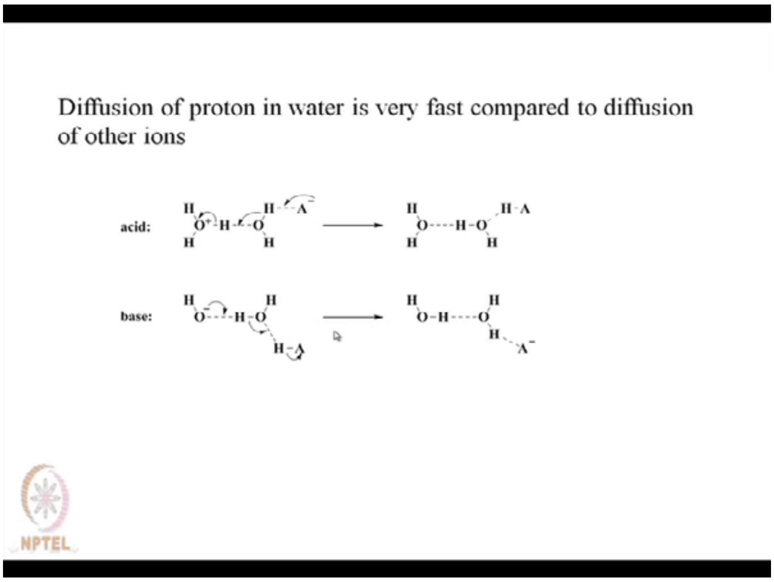

Diffusion of proton in water is very fast compared to diffusion of other ions

Diffusion of proton in water is very fast compared to diffusion of other ions. Why? because proton is very small in size and as a result of which and also there is A there is A mechanism which is called it is A Grotus type mechanism by which basically proton does not need to you know, swim close to your interacting entity. What happens is that it is basically a relay kind of mechanism that that 1 side this proton is attaching next side another proton is detaching. In this way, this proton is attaching over here say at one point. So, next point the other proton is detached to another point; so basically, all the proton is attached to this point. But, effectively this the other proton which has been detached has attached to another side. Basically, it is A it is A2 you know to step all though, in order to that the proton original proton required more time to attach to here because, it needed to swim to this position. So, that is why it is a relay kind of mechanism; so it looks like this.

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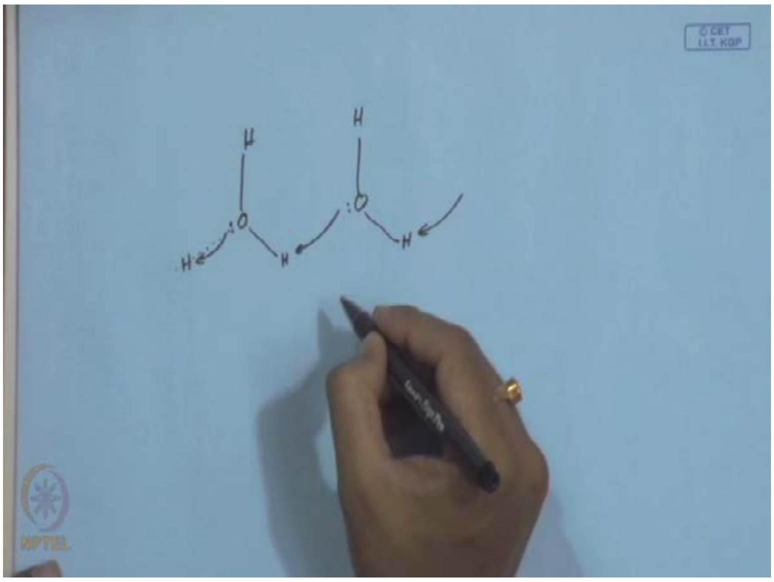

Supposing I have got water so there is another water and you have got 1 proton so the lone pair so it attaches over here this lone pair is snatching this so another lone pair is snatching this effectively this hydrogen bond or this bond has been found. But, see this proton as if has moved to this position. So, it is a kind of push-pull kind of mechanism it is also called grotthuss type of mechanism. That is why it is very fast compared to diffusion of other ions; because, for other ions since it is you know for proton, it is a lightest entity. So, lightest entity means it does not require that much of time to you know, move and also if this mechanism is operative. Then, it is even faster but, for other ions since they are heavier and also maybe because of salvation, they become larger in size. So, what happens that in order for them to diffuse in order to diffuse from one position to another? They would require more time; so that is why diffusion of proton in water is very fast compared to diffusion of other ions.

Now, see it is basically an ion as I told you that here this also shown in the same way why it is faster that you have got a minus which attaches to this proton and then, this bond is broken and is given to here. And then, what happens is that this original this OH bond O plus H bond is. Now, broken so effectively this proton has been taken from here but, effectively as if the proton from here has been taken so net there is A2 step jump although for other ions like say heavier ions this does not happen so this way this is for an acid and for base you see that OH minus it is snatching this proton and effectively as if this proton has been snatched through this water through this water hydrogen bonding.

That is why this is very fast and also since proton is the lightest entity. Therefore, they do not take that much of time to diffuse from one place to another.

Proton transfer involving carbon acid or carbon basis, one example is given here that C H 3 C H2 N O 2. So, water forward reaction, so forward reaction is basically this hydrogen has been taken this hydrogen is taken and H2 plus is generated and then it is A, you know, residence hybrid. Of these two effectively what happens is that all there is A C minus. Now, it is it is converted to in O minus, so initially it was it was a carbon acid. Now, maybe it is converted to oxygen acid maybe it looks like A. Now, as if this hydrogen has been has been taken from here another example is like this C H 3 C O C H to C O C H 3. So, forward reaction I mean, forward process you see that it is you know enolization step. It is your (( )) so basically, this hydrogen is given here. I mean, this hydrogen is switched from here to here 1 2 3 1 3 shift. So, making this double bond then OH and then this OH what happens that this OH makes A makes A hydrogen bonded structure. I mean, 6 membered hydrogen bonded structure. So, although this is slower but, this process I mean, this process is faster the forward process is slower. But, from here to here, this back process is faster and also this forward process is faster because you see but, this two these two are carbon acid and these 2 to 3 it is an oxygen acid. Therefore, this process is faster probably because of this hydrogen 1 formation. So, hydrogen bond makes the process faster compared to when there was no hydrogen bond.

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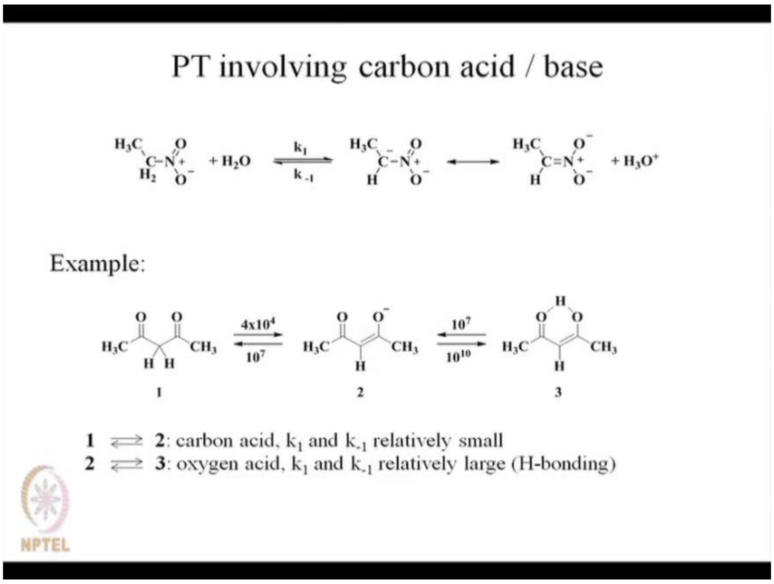

PT involving carbon acid / base

Example:

$1 \rightleftharpoons 2$: carbon acid, k_1 and k_{-1} relatively small
$2 \rightleftharpoons 3$: oxygen acid, k_1 and k_{-1} relatively large (H-bonding)

Here, it is the proton transfer involving I mean, carbon. It is A proton transfer involving oxygen; so it is an oxygen acid. This is A carbon acid; so slow proton transfer and here it is the fast proton transfer; as I told you here proton transfer you know nitrogen oxygen sulfur is faster compared to carbon. Now, we will. Now, concentrate on to the effect of pH on A reaction rate since it is you know, hydrogen mediated I mean, hydrogen plus proton mediated I mean, proton catalyzed reaction or maybe which minus catalyzed reaction.

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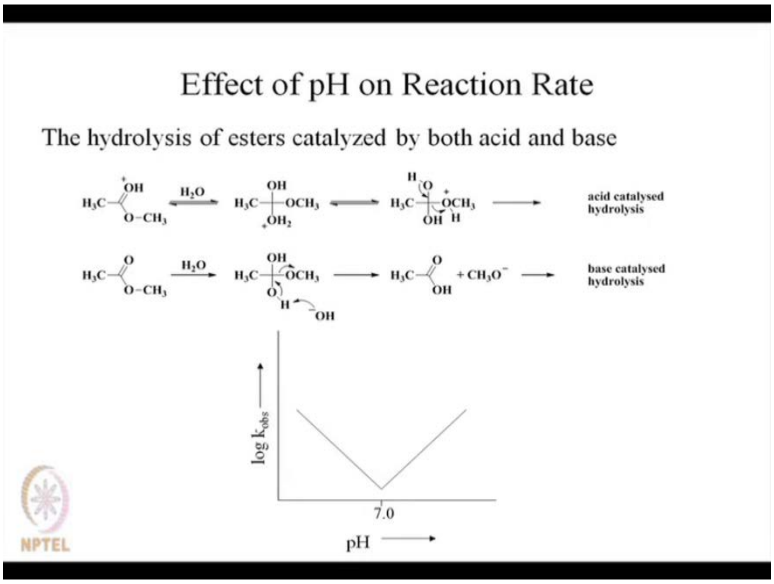

Effect of pH on Reaction Rate

The hydrolysis of esters catalyzed by both acid and base

Let us look into hydrolysis of ester catalyzed by both acid and bases In 1 case let us concentrate on to acid catalyzed and the other case concentrate on to base catalyzed. So, acid catalyzed reaction so you see that this one C H 3 C O O C H 3. So, protonation form it is the protonated form acid catalyzed reaction. So, in presence of water it is A tetrahedral intermediate is formed and then, back firing of this OH electron OH pair then expel of this C H3O H C H3O H means it is methanol. So, it is the acid catalyzed prescription, what about the base catalyzed prescription, you start with C H 3 C O O C H 3 and water in presence of water. Also, in presence of A base; so this in presence of water this tetrahedral intermediate is formed and then OH minus (( )) then this one is expelled as O C H 3 minus. So, then it is C H 3 C H3O o C O OH. Now, then in presence of in presence of water in presence of water I mean, this is the equilibrium has been shifted from C H3O minus to C H2 OH and C H 3 C O O minus.

But, it is A base catalyzed prescription and if we plot logarithm of key observed rate constant as A function of pH approximately you know the rate is found to be I mean, it is found that at pH 7. That is A neutral pH its rate is minimum so either of if it is increased this way I mean, if it is going this way acidic region or may be in the basic region. So, the reaction rate is increasing so this particular reaction that is particular reaction means the acid catalyzed or base catalyzed hydrolysis of ester so when pH is 7 and there is neutral pH it is A minimum rate and if you go either way whether you increase the pH or whether you increase that. I mean, decrease in the pH rate is increased because it follows such A mechanism; because it has got two options and that is acid catalyzed option or may be the base catalyzed option. So, both way I mean, if you go this way or that way the rate of reaction increases. Thus, we can see that there is there is A you know, great deal of effect of pH on such kind of reaction.

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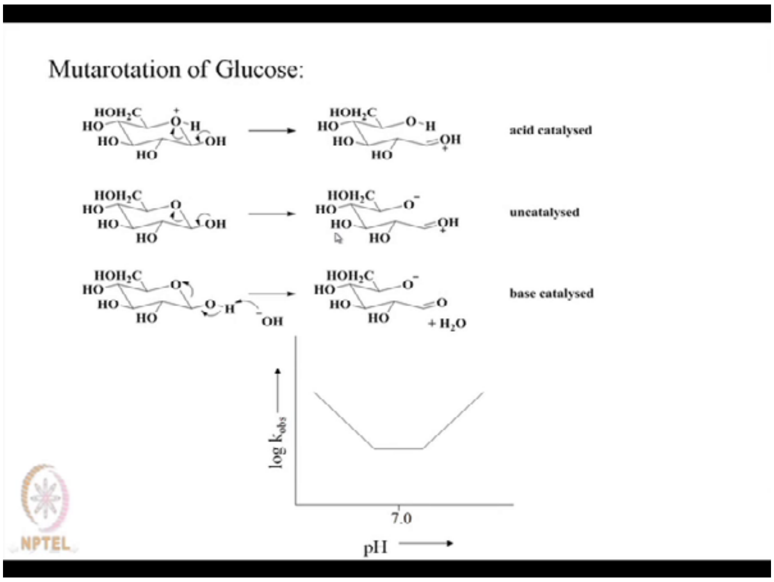

Mutarotation of Glucose:

Next, another example is an interesting example. Mutarotation of glucose: it is you know cyclic form of glucose. Now, if it is acid catalyzed reaction then, we see that this is the prescription this is for uncatalyzed one. This is uncatalyzed prescription and this is base catalyzed prescription. Now, if we plot log key observed versus pH then, around neutral pH the rate is minimum and not exactly at 7 but, around pH 7. Now, so for A region I mean, for some range of pH in the vicinity of 7 it is flat and then it increases this way also and also this way because of this mechanism. So, you know this is ring opening reaction; that is, you know 6 membered closed structure to an open structure and this is acid catalyzed mode. This is uncatalyzed and this is very slow, this is very slow and this one is base catalyzed one because importantly you know you see here this OH minus snatches this proton from this anomeric carbon and then this carbon will bond is found and then, this is open here. Since, there is no such OH minus or may be no such proton because it is you know at pH around 7 uncatalyzed means around 7.

In neutral pH, the concentration of H plus or OH minus is you know I mean, these are very low. So, under such low concentration means either mechanism or this mechanism or that mechanism is difficult to operate so maybe there is A very little amount of H plus which tends to protonated this oxygen but, since concentration is less that contribution is also less in the same (( )) OH minus also less. So, contribution of this step is also less but, it is happening because there is A although it is very low but, there is it is it is finite it has got some finite value. So, with that finite value of OH minus R H plus this reaction proceeds I mean, this step proceeds but, with you know you know rate much reduced so in the vicinity of pH 7 you see that it is flat it increases further in the right hand side and also in the left hand side like the example I gave in the earlier slide that you know that for hydrolysis of ester catalyzed by acid or base.

In the same way, for uncatalyzed reaction like there is 1 step it could happen over here but, that happens very slowly. That is why because, H plus and OH minus is less at pH 7. So, that is why it is minimum; rate is minimum and you can study this mutarotation reaction. You know polar metrically; so in 1 case you use acid, another case you use base and the third case you do not use acid or base or basically you use A you know pH 7 buffer. May be, where the concentration of H plus or concentration of OH minus will be very low and you can polar metrically study and you can find out the rate because, with time your optical rotation changes and from this change in optical rotation you can find out this observed k.

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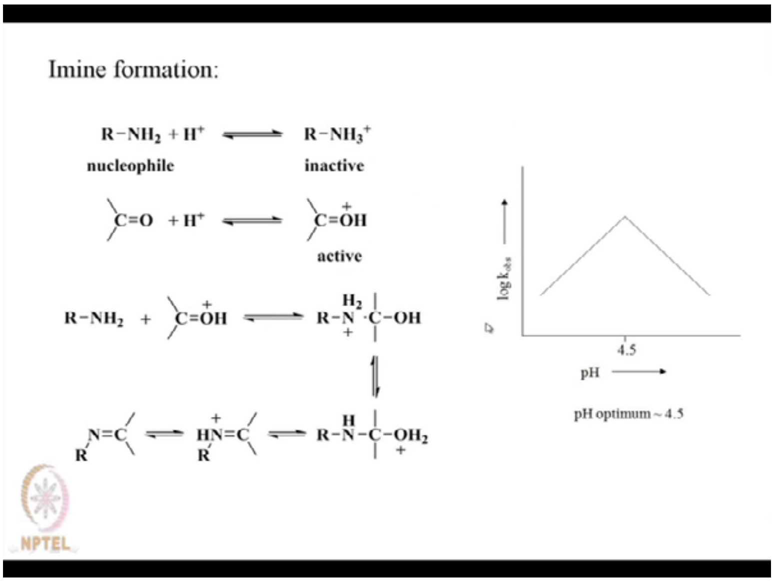

Imine formation:

$R{-}NH_2 + H^+ \rightleftharpoons R{-}NH_3^+$

nucleophile inactive

$>C{=}O + H^+ \rightleftharpoons >C{=}\overset{+}{O}H$

active

$R{-}NH_2 + >C{=}\overset{+}{O}H \rightleftharpoons R{-}\overset{+}{N}H_2{-}C{-}OH \rightleftharpoons R{-}NH{-}C{-}\overset{+}{O}H_2 \rightleftharpoons R\overset{+}{H}N{=}C< \rightleftharpoons RN{=}C<$

pH optimum ~ 4.5

Next is, there is another reaction which is Imine formation. You see, if you plot log k observed versus pH it is found to be to maximize around pH 4 point 5 to 5. So, optimum pH is around 4 point 5. So, if you go either way like if you go below 4 point 5 or maybe above 4 point 5 reaction has been found a rate has been found to be reduced. So, what happens is that in presence of an acid and that is in presence of H plus in presence of H plus. So, this forms R N H 3 plus so it is inactive although it is the nucleophile but, it is inactive. But, in presence of H plus this carbonyl it gets protonated and it is further activated and then R N H2 attacks this one to produce this one and then it equilibrate here and then this bond I mean, this bond (( )) this is a living group O H2 plus is a good ( ) group so it (( )) and then it forms Imine and it has been found to have, your rate has been found to maximum value when we are in the vicinity of 4 point 5 to 5. So, like I mean, unlike this one where you are getting a plot around 7; although, in this case you are getting a minimum around 7 but, here the maxima you do you are getting at for some at a value which is different from 7 that is 4 point 5 to 5. So, this is another example of you know, acid catalysis and you see acid catalysis is an also the effect of pH. So, from these 3 examples we can say that the reactions which are catalyzed by acid I mean, H plus they these may have you know you know strong dependence of pH.

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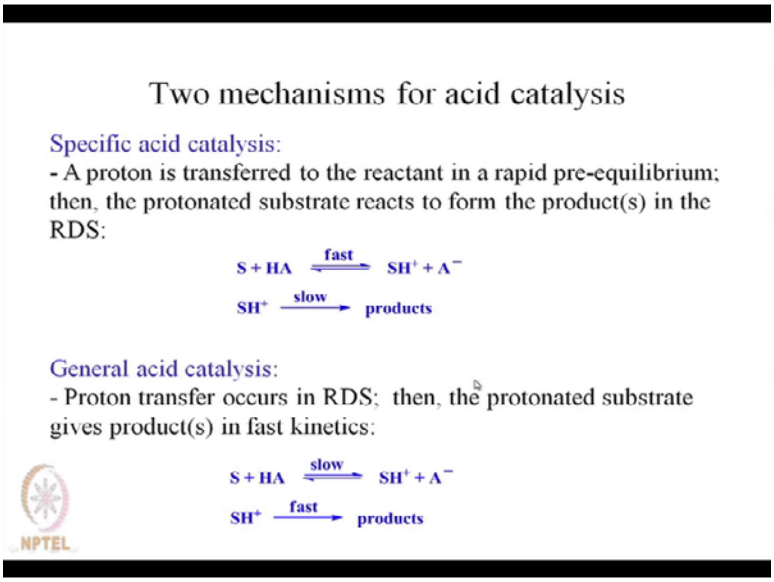

Two mechanisms for acid catalysis

Specific acid catalysis:

- A proton is transferred to the reactant in a rapid pre-equilibrium; then, the protonated substrate reacts to form the product(s) in the RDS:

$$S + HA \xrightleftharpoons{\text{fast}} SH^+ + A^-$$

$$SH^+ \xrightarrow{\text{slow}} \text{products}$$

General acid catalysis:

- Proton transfer occurs in RDS; then, the protonated substrate gives product(s) in fast kinetics:

$$S + HA \xrightleftharpoons{\text{slow}} SH^+ + A^-$$

$$SH^+ \xrightarrow{\text{fast}} \text{products}$$

Next, let us look into mechanisms of acid catalysis. So, one is you know which is called as specific acid catalysis and the other one is called the general acid catalysis. For the first one that is, specific acid catalysis what is happening, A proton is transferred to the reactant in a rapid pre-equilibrium like this. This is your substrate or reactant HA; so this A I mean, this HA this proton is transferred to this S producing S H plus and then this is a fast equilibrium. This equilibrates very fast and then once it is formed this S H plus it slowly gives rise to products. So, this is fast equilibrium then slow product formation. This is the rate determining step and for your general acid catalysis. In that case, the reverse is the situation that proton transfer occurs in the rate determining step so there is the equilibration states the slow step and then once S H plus is formed it produces I mean, it gives rise to products very fast so for specific one it is the first fast pre-equilibrium and for the general acid catalysis it is the slow equilibration I mean, slow proton transfer. These are the two situations one is your specific acid catalysis and other one is the general acid catalysis.

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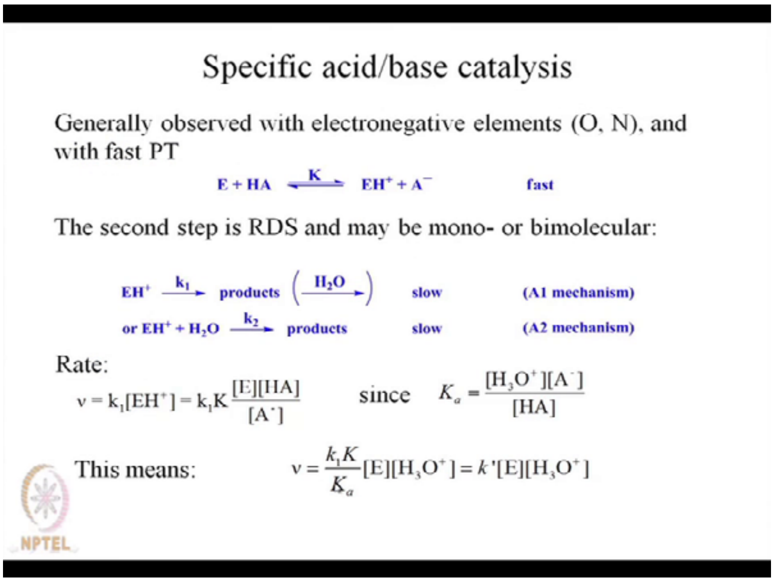

Specific acid/base catalysis

Generally observed with electronegative elements (O, N), and with fast PT

$$E + HA \underset{}{\overset{K}{\rightleftharpoons}} EH^+ + A^- \qquad \text{fast}$$

The second step is RDS and may be mono- or bimolecular:

$$EH^+ \xrightarrow{k_1} \text{products} \left(\xrightarrow{H_2O}\right) \qquad \text{slow} \qquad \text{(A1 mechanism)}$$

$$\text{or } EH^+ + H_2O \xrightarrow{k_2} \text{products} \qquad \text{slow} \qquad \text{(A2 mechanism)}$$

Rate:

$$v = k_1[EH^+] = k_1K\frac{[E][HA]}{[A^-]} \qquad \text{since} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

This means: $$v = \frac{k_1K}{K_a}[E][H_3O^+] = k'[E][H_3O^+]$$

So, specific acid base catalysis; let us look into it again. It is generally observed with electronegative elements as I told you at the very start of our discussion that you see here for your specific acid catalysis this one is fast; that is, the proton transfer is fast. So, proton transfer fast means it is expected to involve oxygen, nitrogen and the proton transfer is very fast. This is the equilibrium constant and the process I mean, this pre-equilibration is very fast and the second step is the rate determining step. It may be mono or may be unimolecular or may be bimolecular. So, for unimolecular case E H plus with rate constant k 1 produces your product and then I mean, in presence of water it gives rise to I mean, products in presence of water. Of course, then it is A slow and unimolecular mechanism. For the other one, you see that water is involved here in this step, in this slow step. That is why it is A bimolecular or it is called the A2 mechanism; so for your rate we see that v is equal to k 1 into E H plus k 1 into E H plus. And E H plus means you see, k E H plus means it is you see that equilibrium constant k is equal to concentration of E H plus divided by concentration of E and concentration of HA.

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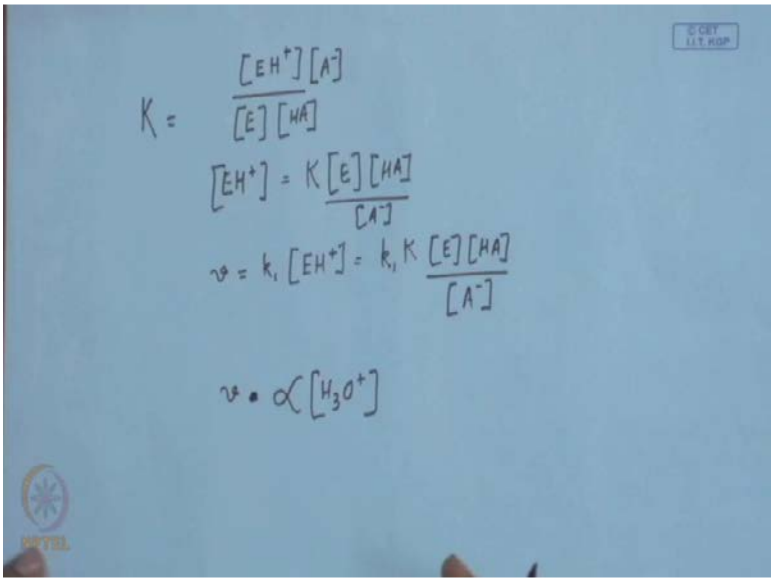

$$K = \frac{[EH^+][A^-]}{[E][HA]}$$

$$[EH^+] = K\frac{[E][HA]}{[A^-]}$$

$$v = k_1[EH^+] = k_1 K\frac{[E][HA]}{[A^-]}$$

$$v \propto [H_3O^+]$$

E H plus is equal to k into E into HA; so you just plug in this you plug in this to your expression that is, v is equal to k O 1 E H plus which is equal to k O 1 into k. Yes, this one will have you know E H plus into A minus of course, so I missed one thing. This is A minus so k k into E HA divided by A minus so this is the rate expression including your equilibrium constant so so since k A is H3O plus A minus divided by HA. So, you can plug in this you can plug in this over here. Ultimately, you get the v is equal to k 1 into k divided by k A into E into H3O plus. So, you see that this rate is strongly dependent on H3O plus concentration; that is, your acid concentration or the concentration of hydronium ion present in the solution in the reaction mixture. We have seen that your rate is dependent on the rate constant for this slower 1 then equilibrium constant for your E HA E H plus A minus equilibrium and also the acid constant k A and you see that v is proportional to H3O plus so v is proportional to H3O plus concentration.

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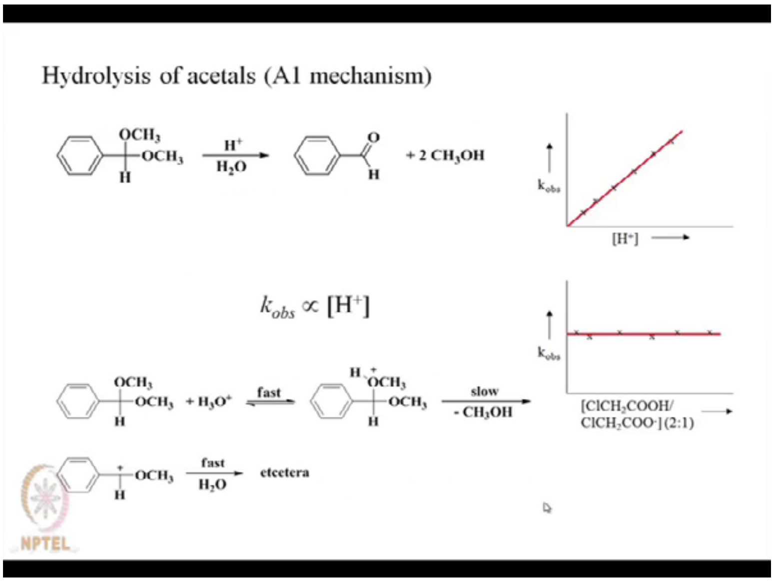

Hydrolysis of acetals (A1 mechanism)

$k_{obs} \propto [H^+]$

Next, let us look into hydrolysis of acetyls unimolecular mechanism, that this is the acetyl then in presence of H plus. Of course, aqueous acid you see that acetaldehyde gives rise to I mean, acetyl of acetaldehyde means I mean, benzaldehyde sorry it is not acetyl it is benzaldehyde so benzaldehyde acetyl then in presence of H plus produces A benzaldehyde and two molecules of C H3O H and you see that in presence of H plus the key observed as H plus is increased your k observed is also increased. It is not exactly linear although it is just giving you an idea of whether k observed is increasing or not you can also have plotted. You can also plot log k observed as a function of you know pH. So, it is you know increasing exactly how much it is increasing what is the exact. So, we are not looking into it you see that k observed is proportional to H plus concentration and what is the mechanism mechanism is that you have got the acetyl of bia cetyl.

So, that is biacetyl of benzaldehyde in presence of H3O plus it is the fast equilibrium and then slow you know, this rupturing of this bond produces products. Again, what you do if you plot k observed as a function of your buffer concentration? Although, keeping your pH constant you would not see any change in your k observed. That means it is strongly depends on its you know this hydrogen ion concentration so this is A 1 mechanism A 1 mechanism; means, your this one fast pre-equilibrium followed by slow decomposition. Here, it is fast pre-equilibrium followed by slow decomposition to your products so in presence of acid this is your acid so here protonation takes place and then the reaction process like this.

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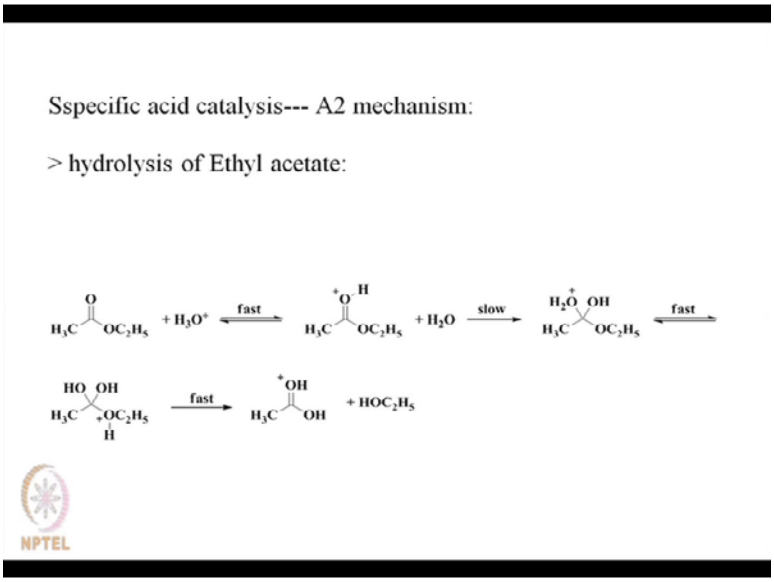

Sspecific acid catalysis--- A2 mechanism:

> hydrolysis of Ethyl acetate:

Next, specific acid catalysis and it is A2 mechanism hydrolysis of ethyl acetate. Ethyl acetate so, again go back to this one in a slow equilibration fast product formation. This one in presence O H3O plus; so this is a your slow equilibrium I mean, fast then slow this is your fast equilibration A2 mechanism; it is A bimolecular. Of course, bimolecular A2 mechanism means here it is a bimolecular one. This one I am looking into this; 1 see it is product formation and here you see that E H plus H2 O k 2 product formation is a is a slow I mean, slow it is A2 mechanism. This is unimolecular; this is your bimolecular so we are now, concentrating on bimolecular you see that it is fast protonation followed by followed by your bimolecular you know bimolecular slow decomposition; hydrolysis of ethyl acetate is of is of such kind.

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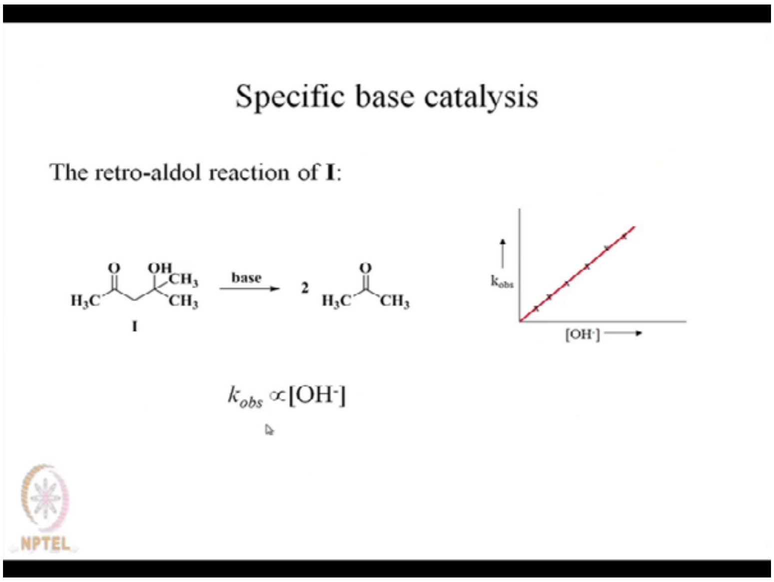

Specific base catalysis

The retro-aldol reaction of **I**:

$k_{obs} \propto [OH^-]$

Now specific base catalysis there is another example retro-aldol reaction of this one in presence of base it produces it produces acetyl. So, it has been found that rate constant k is proportional to OH minus concentration and it increases linearly I mean, there is a positive slope like your this reaction this one is an H plus catalyzed; this is OH minus catalyze is a specific base catalysis.

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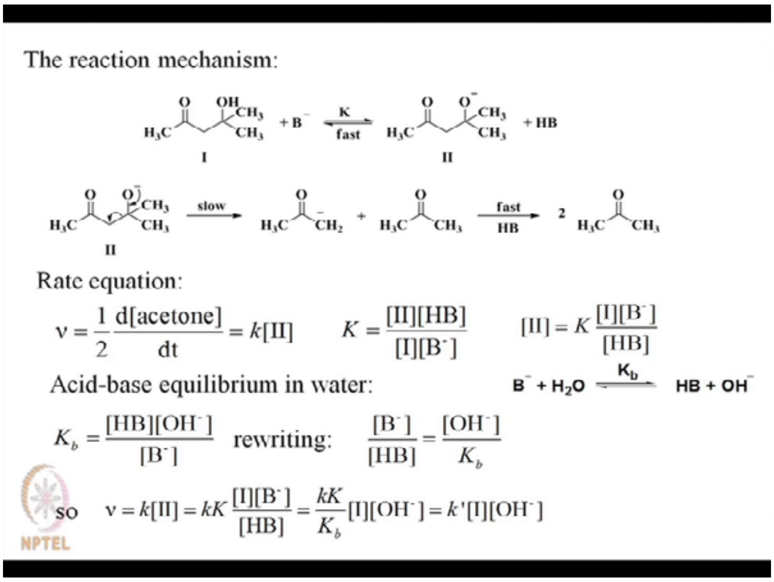

The reaction mechanism:

Rate equation:

$$v = \frac{1}{2}\frac{d[\text{acetone}]}{dt} = k[\text{II}] \qquad K = \frac{[\text{II}][\text{HB}]}{[\text{I}][\text{B}^-]} \qquad [\text{II}] = K\frac{[\text{I}][\text{B}^-]}{[\text{HB}]}$$

Acid-base equilibrium in water: $B^- + H_2O \xrightarrow{K_b} HB + OH^-$

$$K_b = \frac{[\text{HB}][\text{OH}^-]}{[\text{B}^-]} \quad \text{rewriting:} \quad \frac{[\text{B}^-]}{[\text{HB}]} = \frac{[\text{OH}^-]}{K_b}$$

so $$v = k[\text{II}] = kK\frac{[\text{I}][\text{B}^-]}{[\text{HB}]} = \frac{kK}{K_b}[\text{I}][\text{OH}^-] = k'[\text{I}][\text{OH}^-]$$

What is the reaction? I mean, what is the reaction mechanism in presence of base it is an equilibration it is fast equilibrium. So, this proton is snatched by B minus producing H B and then this slow decomposition show this electron I mean, this charge is back fired and then this bond is ruptured so producing this two and then ultimately from water it takes up 1 proton to give rise to molecules of acetone. Now, rate of rate equation rate of reaction is half D acetone D T there is a rate of formation of acetone and ultimately, if we follow this you know expressions k equal to 2 divided 2 into H B divide by 1 into B minus and then concentration of 2 will be this one is 1 this one is 2. So, concentration of 2 has got this expression and considering acid base equilibrium in water B minus plus water k B H B and O minus so if we plug in the appropriate number I mean, expression over here then we will be seeing like the other 1 that is your hydrolysis of ester let us go back to that slide also you see that v is proportional to H3O plus. In the same way, here we are also getting your v is proportional to OH minus. So, it is a specific base catalysis where we are seeing that your reaction rate reaction rate I mean, k observed is very much proportional to OH minus.

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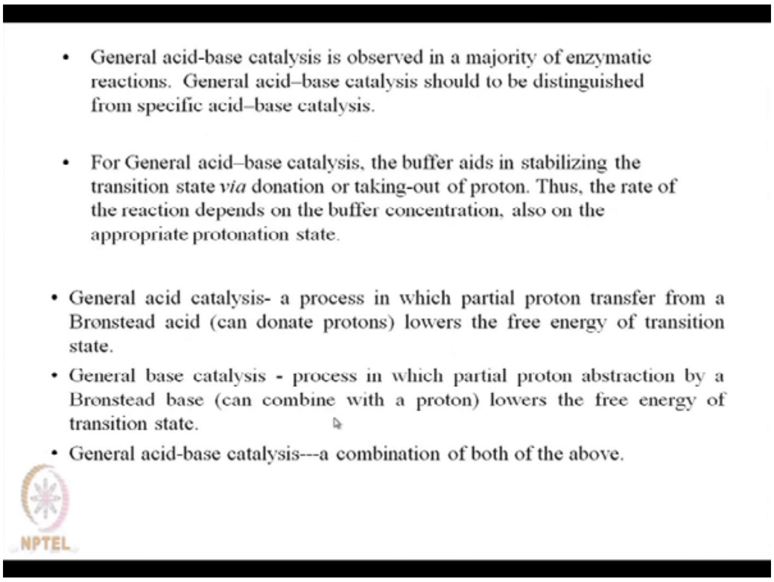

- General acid-base catalysis is observed in a majority of enzymatic reactions. General acid–base catalysis should to be distinguished from specific acid–base catalysis.
- For General acid–base catalysis, the buffer aids in stabilizing the transition state *via* donation or taking-out of proton. Thus, the rate of the reaction depends on the buffer concentration, also on the appropriate protonation state.
- General acid catalysis- a process in which partial proton transfer from a Bronstead acid (can donate protons) lowers the free energy of transition state.
- General base catalysis - process in which partial proton abstraction by a Bronstead base (can combine with a proton) lowers the free energy of transition state.
- General acid-base catalysis---a combination of both of the above.

Now, general acid base catalysis is observed in a majority of enzymatic reactions general acid base catalysis should be distinguished from specific acid base catalysis for general acid base catalysis the buffer aids in stabilizing the transition state via donation or taking out of proton thus the rate of reaction depends on the buffer concentration for general acid base catalysis and also on the appropriate protonation state general acid catalysis A process in which partial proton transfer from a bronsted acid which can donate protons, lowers the free energy of transition state general base catalysis process in which partial proton abstraction by a bronsted base. That is, which can combine with a proton and lowers the free energy of transition state and general acid base catalysis in case of a general acid base catalysis you know I mean, original acid base catalysis, a combination of both can also happen. General acid base catalysis it is a general acid catalysis and it is A base catalysis of so far general acid base catalysis both of these two can happen.

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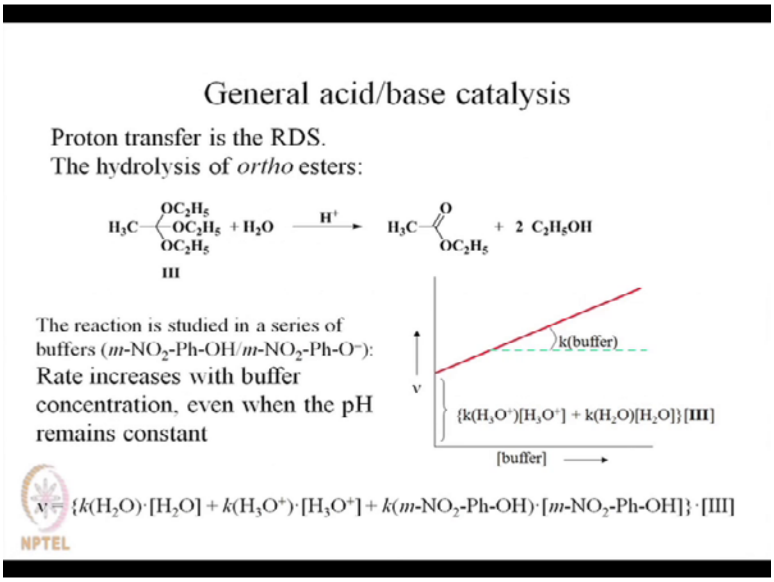

General acid/base catalysis

Proton transfer is the RDS.
The hydrolysis of *ortho* esters:

$$H_3C-C(OC_2H_5)_3 + H_2O \xrightarrow{H^+} H_3C-C(=O)OC_2H_5 + 2\ C_2H_5OH$$

III

The reaction is studied in a series of buffers (m-NO_2-Ph-OH/m-NO_2-Ph-O^-):
Rate increases with buffer concentration, even when the pH remains constant

$$v = \{k(H_2O)\cdot[H_2O] + k(H_3O^+)\cdot[H_3O^+] + k(m\text{-}NO_2\text{-Ph-OH})\cdot[m\text{-}NO_2\text{-Ph-OH}]\}\cdot[III]$$

NPTEL

Next general acid base catalysis proton transfer is the rate determining step as for example, hydrolysis of ortho esters in presence this is 3 number 3 so in presence of H plus it gives rise to this and this type of reaction has been studied in a series of buffers that is phenol kind of phenol phenoxide buffer and it has been found that rate increases with buffer concentration even when the pH remains constant so your rate of reaction rate is k corresponding to water with constant for water then rate constant for H3O plus and then rate constant for your the one which is coming from pH OH that is phenol so and also the concentration of phenol so these three are the are the contribution of the different constituent studies water H3O plus and also from your buffer and this is the reactant but, this k part k part has got the contribution from k part has got the contribution from your water that is which is present in large axis and also, if there is some H3O plus ions present and also on this three. But, here if we plot v versus buffer concentration you see that it starts from somewhere over here. If you increase the buffer concentration rate has been found to increase from here to here. So, this part you can call the residual one which is the contribution from your H3O plus part and also from your H2O part.

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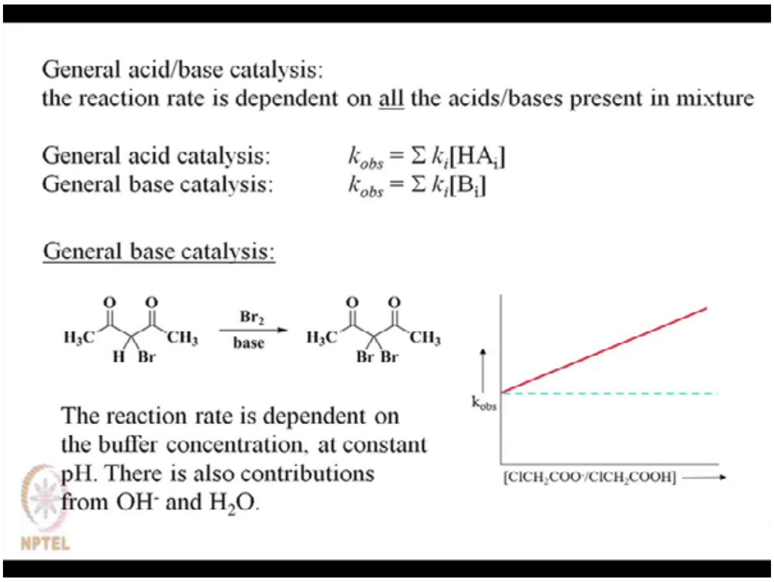

General acid/base catalysis:
the reaction rate is dependent on all the acids/bases present in mixture

General acid catalysis: $k_{obs} = \Sigma k_i[\mathrm{HA_i}]$
General base catalysis: $k_{obs} = \Sigma k_i[\mathrm{B_i}]$

General base catalysis:

The reaction rate is dependent on the buffer concentration, at constant pH. There is also contributions from OH^- and H_2O.

Next slide, general acid base catalysis the reaction rate is dependent on all the acid bases present in a mixture as I told you that this is A. Maybe, this is A base this is acid and this is also an acid so that is why all of contribution from all of them is in action so for general acid catalysis contribution of all the HA is present and for general base catalysis contribution from all the bases present in the mixture so observed you know k is the contribution from your individual is the contribution from your individual acids or individual bases. An example of general base catalysis you see that bromination of this one debromination the second bromination in presence of this. so, observed rate constant has been found to increase with your buffer concentration even if you fix the pH. So, this reaction that is dependent on the buffer concentration at constant pH and there is although there is a contribution of OH minus and H2O so this part is accounting for this line that is there is also contributions from OH minus and water. Thus, for general acid base catalysis, what happens? That rate of reaction depends on the buffer concentration as well which is evident from your this part is from your from your this last sentence that is there is also contributions from OH minus and H2O.

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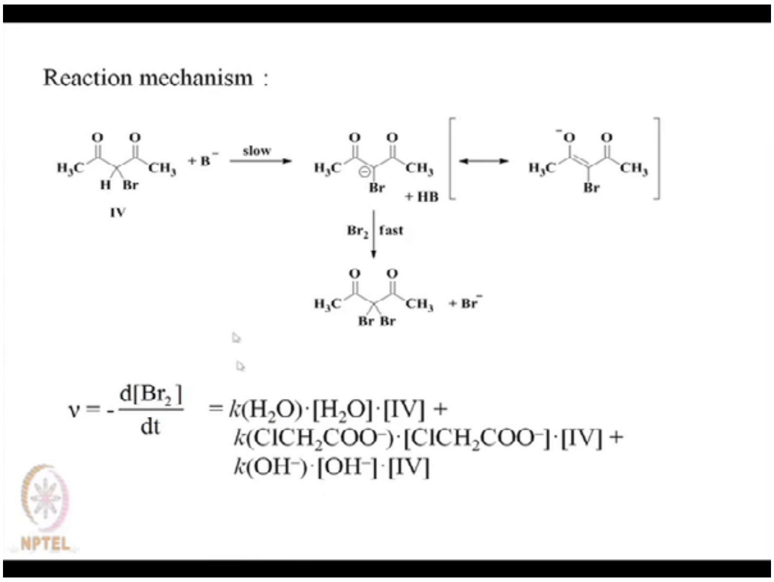

Reaction mechanism :

$$\nu = -\frac{d[Br_2]}{dt} = k(H_2O)\cdot[H_2O]\cdot[IV] + k(ClCH_2COO^-)\cdot[ClCH_2COO^-]\cdot[IV] + k(OH^-)\cdot[OH^-]\cdot[IV]$$

Now, reaction mechanism goes like this that is reaction mechanism for this particular reaction you know it is shown over here that is it is a slow abstraction of proton and then it has got the resonance hybrid then in presence of bromine you know this minus attacks the bromine to snatch this B R and B R minus is you know dispersed.

So rate of rate of disappearance of B R 2 which is which has got the contribution from your water it has got the contribution from your OH minus and it has also got the contribution from your this one since it is a general base catalysis so this base is also effective over here. So, contribution that is your k arising out of that is the contribution of this k due to this C L C H2 C O minus or maybe, the contribution of this to your k - overall k for this water and this is your contribution to overall k for your OH minus so these are individual contributions.

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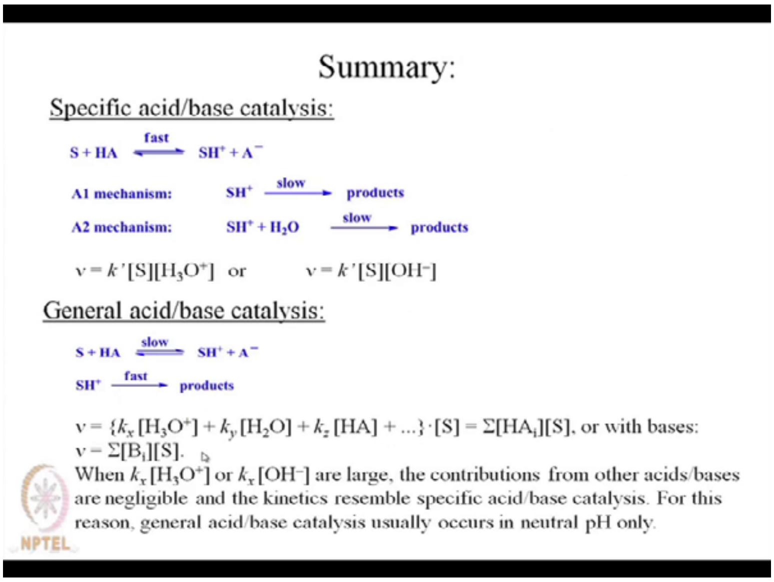

Summary:

Specific acid/base catalysis:

$$S + HA \overset{fast}{\rightleftharpoons} SH^+ + A^-$$

A1 mechanism: $SH^+ \xrightarrow{slow} products$

A2 mechanism: $SH^+ + H_2O \xrightarrow{slow} products$

$v = k'[S][H_3O^+]$ or $v = k'[S][OH^-]$

General acid/base catalysis:

$$S + HA \overset{slow}{\rightleftharpoons} SH^+ + A^-$$

$$SH^+ \xrightarrow{fast} products$$

$v = \{k_x [H_3O^+] + k_y [H_2O] + k_z [HA] + \ldots\} \cdot [S] = \Sigma[HA_i][S]$, or with bases:
$v = \Sigma[B_i][S]$.

When $k_x [H_3O^+]$ or $k_x [OH^-]$ are large, the contributions from other acids/bases are negligible and the kinetics resemble specific acid/base catalysis. For this reason, general acid/base catalysis usually occurs in neutral pH only.

Next, summary specific acid base catalysis so you see here S plus HA is a fast equilibration S H plus A minus so the mechanism is A 1 mechanism that is uni molecular mechanism S H plus slow giving rise to products or bimolecular mechanism S H plus water to products. It is A slow process so for specific acid or specific base catalysis you see that rate of the reaction velocity of the process as you know has this kind of expression and you where you can see that your velocity is proportional to H3O plus or maybe velocity is proportional to OH minus. So, that means, it has got the direct dependence on your acid concentration or base concentration so it is A it is thus it is specific acid or specific base catalysis.

General acid base catalysis on the other hand, it is slow equilibrium and then fast dissociation to products and here your overall here you know, the velocity of the reaction it is from, it has got the contribution from various components like H3O plus H2O then HA or maybe with bases it is OH minus H2O and A minus. It is basically sum over various factors sum over various you know various concentration terms.

Now, when the concentration of this concentration of this H3O plus or OH minus. so you see it is it is as these are large then contribution from other acids bases are negligible that means in case of general acid base catalysis you see that the overall velocity of the reaction is proportional to you know contribution coming from H3O plus or plus contribution coming from water and also from the HA that is from the acid but, suppose out of this three, if we make this one large then contributions of these are negligibly small or if you make this OH minus very large contribution of this one very large then, contributions of other parts are negligibly small and the kinetics resembles specific acid base catalysis. Then, your expression is converted; that is this expression is converted to this expression. Or maybe, this expression depending on whether it is a base catalyze I mean, acid catalyst or it is a base catalyzed cases.

That is why you know general acid base catalysis usually occurs in neutral pH or maybe around pH neutral situation. So, that means you can convert a general acid I mean, general acid base catalysis to A specific acid base catalysis by taking your base or your acid to a large extent. That is, if you can make their contribution large then the contribution from water or contribution from HA or maybe contribution from you know a minus these are becoming negligibly small and it is A and your situation gets converted from general to specific.

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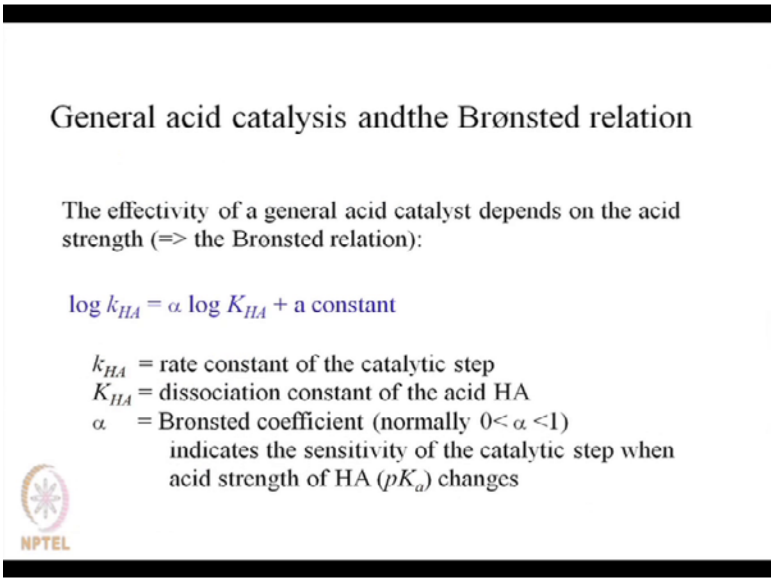

General acid catalysis andthe Brønsted relation

The effectivity of a general acid catalyst depends on the acid strength (=> the Bronsted relation):

$\log k_{HA} = \alpha \log K_{HA}$ + a constant

k_{HA} = rate constant of the catalytic step
K_{HA} = dissociation constant of the acid HA
α = Bronsted coefficient (normally $0 < \alpha < 1$) indicates the sensitivity of the catalytic step when acid strength of HA (pK_a) changes

General acid catalysis and the bronsted relation the affectivity of a general acid catalyst depends on the acid strength and that is the bronsted relation; I mean, we relate this to bronsted relation. That is, log k HA is equal to alpha log k HA; that is A equilibrium constant plus some constant. So, k H is the rate constant for the catalytic step that is a step which is which is thought to be the you know the step where in, your catalysis occurs. k H is the dissociation constant of the acid alpha is the bronsted coefficient and normally, it is in the range of 0 to 1. 0 is less than alpha is lesser than 1 and this indicates the sensitivity of the catalytic step when acid strength of HA. That is, P k changes; so it is A marker for the sensitivity and it is called the bronsted coefficient.

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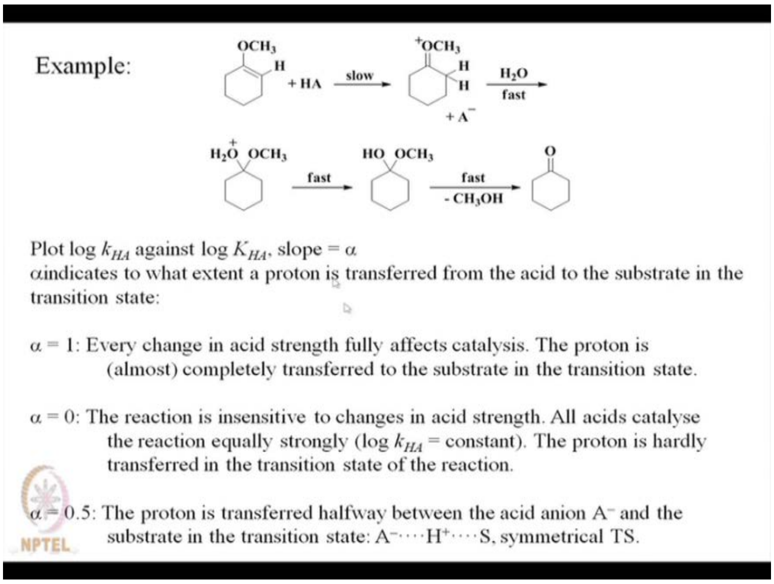

Example:

Plot log k_{HA} against log K_{HA}, slope = α

αindicates to what extent a proton is transferred from the acid to the substrate in the transition state:

$\alpha = 1$: Every change in acid strength fully affects catalysis. The proton is (almost) completely transferred to the substrate in the transition state.

$\alpha = 0$: The reaction is insensitive to changes in acid strength. All acids catalyse the reaction equally strongly (log k_{HA} = constant). The proton is hardly transferred in the transition state of the reaction.

$\alpha = 0.5$: The proton is transferred halfway between the acid anion A^- and the substrate in the transition state: $A^- \cdots H^+ \cdots S$, symmetrical TS.

This is the expression that is log k HA is equal to alpha log caps k HA plus constant so we will try to use this expression. Example: this is reaction. Look into this reaction this; is slow you know protonation. Then, in presence of water fast dissociation I mean, fast product formation to give you this one, if you plot A log k HA against log equilibrium constant that is this expression, if you plot this with this then you will be getting alpha from your slope and alpha indicates to what extent proton is transferred from acid to the substrate in the transition state. So, that is you know if it is you know slope is unity then situation will be 1 if it is 0 then situation will be another if it is in between like point five. Then situation will be something else also, let us let us look into that when alpha is equal to 1. So, every change in acid strength fully affects catalysis that means, if alpha is 1 that is log k HA it is a rate this is equilibrium constant. So, there is 1 - just 1 to 1 correspondence. Every change in acid strength fully affects catalysis the proton is almost completely transferred to substrate in the transition state you can think in that way alpha is equal to 0 the reaction is insensitive to changes in acid strength alpha is equal to 0 means log k HA is just constant.

So all acid catalyze I mean, all acid catalyze the reaction equally strongly; that means, there is no difference in P k; I mean, there is no difference with respect to P k any acid can do the reaction. That is why it is called all acids catalyze the reaction equally strongly. So, log k HA is constant the proton is hardly transferred in the transition state of the reaction and if it is point five that means, if it is log k H is equal to point five log capital k HA plus constant. Then it is called the proton is transferred halfway between the acid anion and the substrate in the transition state; so transition state is symmetrical it looks like this.

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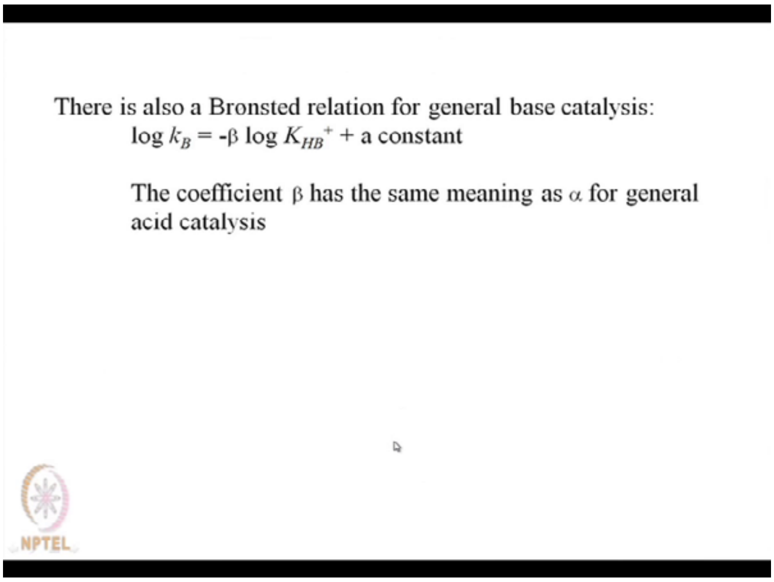

There is also a Bronsted relation for general base catalysis:

$$\log k_B = -\beta \log K_{HB^+} + \text{a constant}$$

The coefficient β has the same meaning as α for general acid catalysis

There is also A similar relation for general base catalysis for bronsted; so it is log k B is equal to minus log k H B plus constant. So, the coefficient beta is has the same meaning as alpha for the general acid catalysis.

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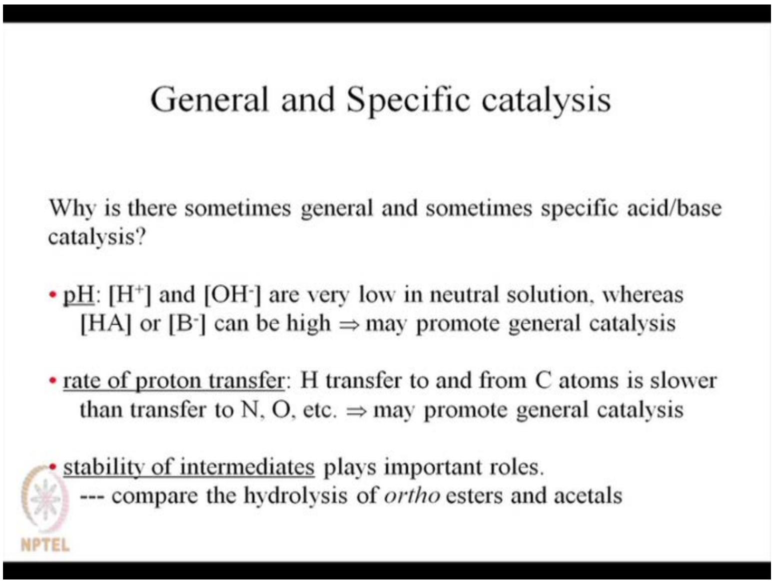

General and Specific catalysis

Why is there sometimes general and sometimes specific acid/base catalysis?

- pH: [H^+] and [OH^-] are very low in neutral solution, whereas [HA] or [B^-] can be high ⇒ may promote general catalysis
- rate of proton transfer: H transfer to and from C atoms is slower than transfer to N, O, etc. ⇒ may promote general catalysis
- stability of intermediates plays important roles.
  --- compare the hydrolysis of *ortho* esters and acetals

So, general and specific catalysis; why is there sometimes general and sometimes specific acid base catalysis? Let us think in terms of pH h plus and OH minus are very low in neutral solution; whereas, HA or B can be high. So, this may promote general catalysis rate of proton transfer H transfer to and from C I means, H transfer to carbon atom or from carbon atom is slower than transfer to nitrogen or oxygen or transfer from nitrogen or oxygen, etcetera. So, this may promote general catalysis stability of intermediates play important roles as for example, compare hydrolysis of ortho esters and acetal.

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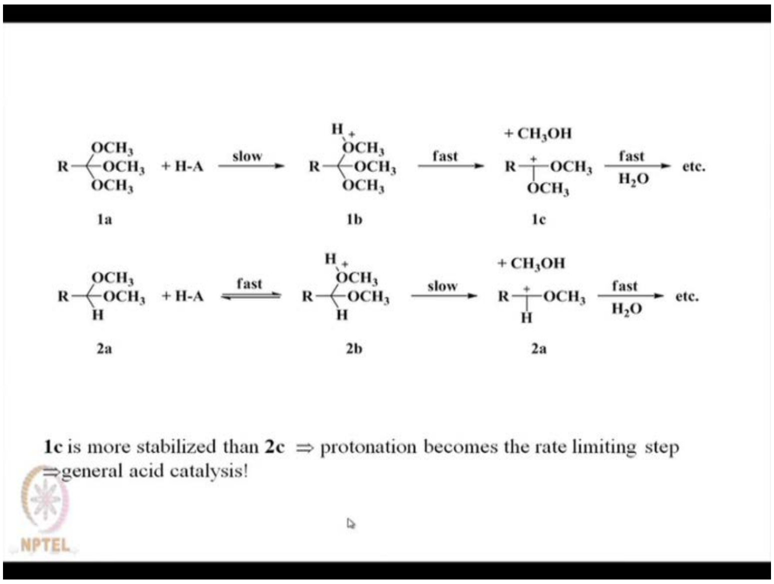

1c is more stabilized than **2c** ⇒ protonation becomes the rate limiting step ⇒general acid catalysis!

This is you know the example; this is the example where you know you see that acetal and ortho ester as I told you, that compare hydrolysis of ortho ester and acetal. So, stability of intermediate plays I mean, plays very important role so if you compare these two you can probably you know think of that 1 C is more stabilized than 2 C. You see, this one this is 2 C this is 1 A 1 B 1 C 2 A2 B 2 C so 1 C is more stabilized than 2 C so protonation becomes the rate limiting step; so this is general acid catalysis.

So, what have we learnt out of this? This acid base catalysis is A; very important you know phenomena. It is observed not only in case of you know general chemical reaction but, also for the biological reactions as well and which we will take over I mean, which we will talk about in the next lecture. but, the thing is that this has got I mean, this acid base catalysis has got two kinds: 1 is specific acid base catalysis and the other case it is general acid base catalysis. So, specific acid base catalysis occurs when we take your acid or base in you know large extent so contribution of you know this parts I mean, other part that is from water or from HA becomes negligibly small and then it is A general acid base catalysis is converted to A specific acid base catalysis. Also, in pH neutral condition the general acid base catalysis is promoted. It is very important that under what condition I mean, what pH condition or what you know? You know buffer condition you are carrying out your reaction is very important.

So, we have learned here this specific acid base catalysis general acid base catalysis, various mechanisms and also the rate schemes and also the effect of pH and the effect of buffer concentration as well. In the next lecture we will talk about this specific or general acid base catalysis for your biological systems I mean, biological reactions and also your metal ion catalyzed reactions. So, that is all for this lecture, thank you.