# Introductory Organic Chemistry

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## Lecture - 22
## Tutorial – 04

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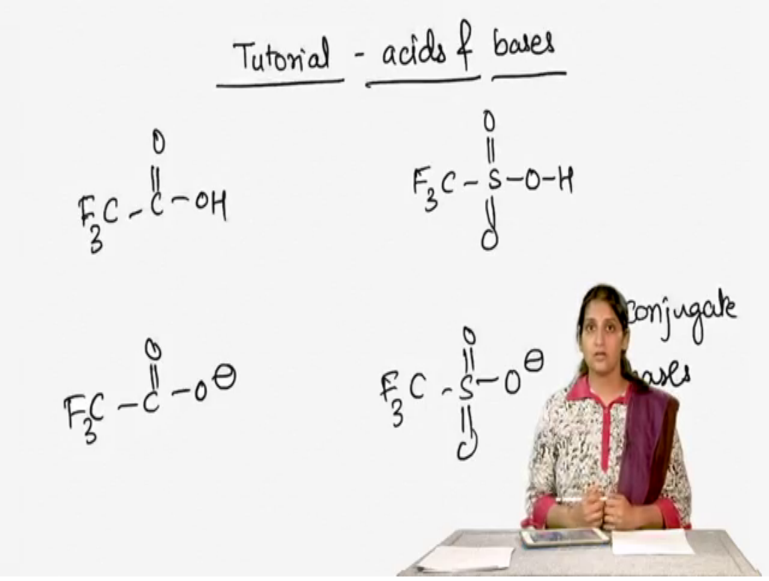

Hello. So, today we are going to start solving the questions on acids and bases. The first question here asks you which one of the following two molecules is more acidic? Okay. So, we have $CF_3COOH$ and we have $CF_3SO_3H$, right. And whenever you are asked with such a question as to which molecule is more acidic and you are asked to compare between two molecules; what you need to do is first write down the conjugate base of the corresponding acid.

So, these are our acidic molecules and we are going to write down their conjugate bases. What we have here is $CF_3COO^-$ and we have $CF_3SO_3^-$, right. So, these are our conjugate bases. Now, the next question you should ask is what is the element in each of the conjugate bases that is bearing the negative charge? If these two are different elements, then you can really compare their stability based on either their size or based on their electronegativity, right. So, these are the two different things that you want to compare.

But right now if you see it is the oxygen atom that is bearing the negative charge in both the cases. So, then how do I decide which one is more stable, right. The reason why we are comparing conjugate bases is as you know, the more stable the conjugate base the stronger is the acid, right. So, now, if you really cannot compare the element that bears the negative charge, the next thing you compare is the possible stability effect due to resonance structures.

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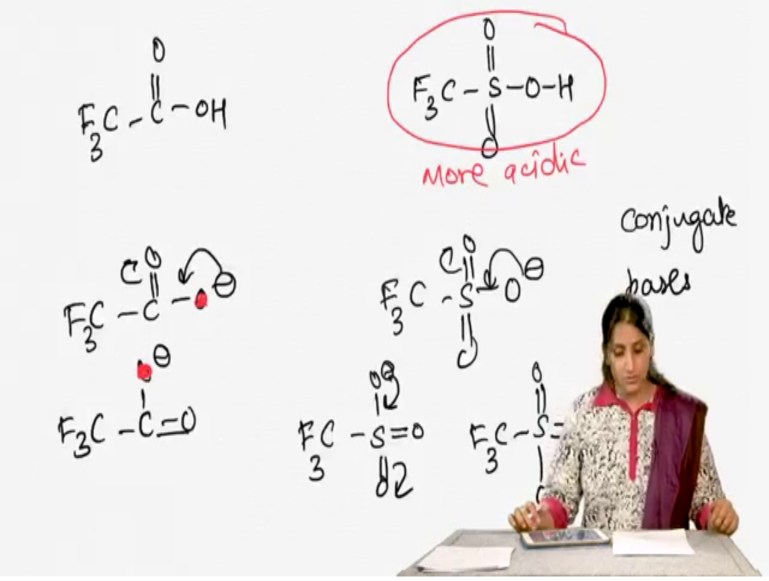

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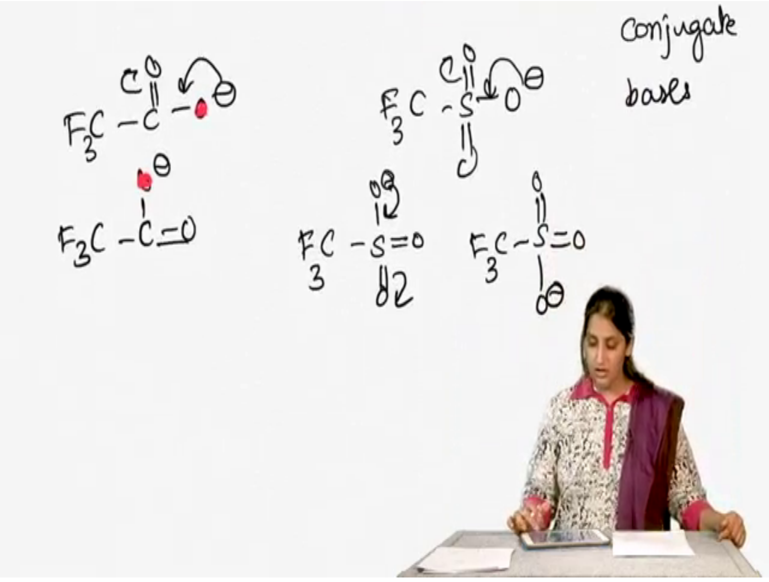

So, now let’s look at the resonance structures; if I really see this I have one resonance structure or one extra resonance structure for $CF_3COOH$ whereas, if I draw a resonance structure here I can draw two possible resonance structures and all of these are valid resonance contributors, right.

So, in one case that negative charge on the Oxygen, this Oxygen for example, can be distributed between two Oxygen atoms, right. So, here you have this Oxygen also sharing that negative charge. So, you can kind of imagine that in the resonance hybrid both the Oxygens will be partially negative; but in this case there are 3 Oxygens that can be partially negative in the resonance hybrid.

So, what happens in the case of $CF_3SO_3H$? The trifluoromethanesulphonic acid; what happens is you can really distribute the charge more such that it goes on more number of Oxygen's thus making this one much more acidic. So the first question is sorted we look at the conjugate bases we say that the conjugate base is more stable due to resonance structure.

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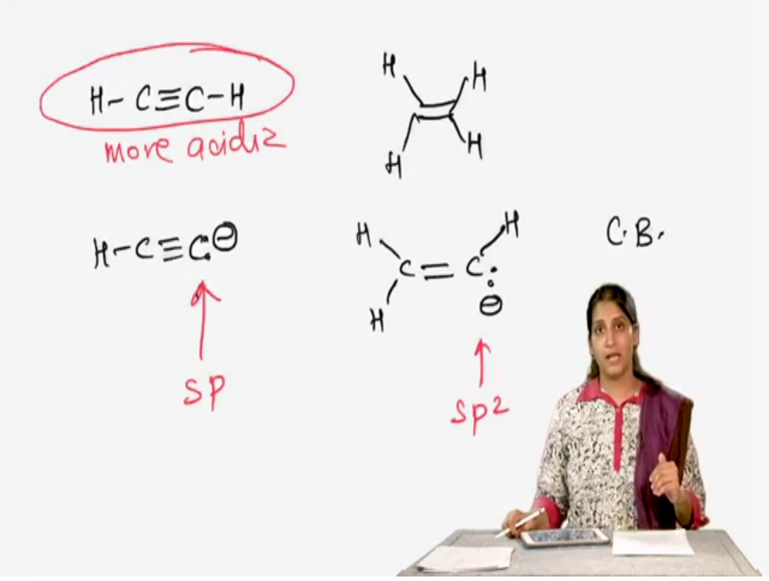

Now, let's go to the next one. The next question talks about, in the following pairs we predict which one is the stronger acid; again, the question is framed on similar lines. So, now, the next pair I have is acetylene versus ethene and if you remember this we also talked about this during our lecture; again what we do is we look at the conjugate bases.

So, I am gonna just write conjugate base henceforth C.B.; if I look at the conjugate base in this case I have a negatively charged carbon; in this case also I have a negatively charged carbon. So, both of these are conjugate bases of these two compounds. Again the first question is what is the element that bears the negative charge, and if you see both of them are carbon. So, we really cannot differentiate based on size or electronegativity, but here is the key. Even though both of them are Carbon they are not the same type of Carbon.

In one case you have sp hybridized Carbon, in the first case; where as in the second case you have $sp^2$ hybridized carbon right. If you really see this, the sp hybridized carbon has more s character in the carbon, right. More s character meaning the electrons are held closer to the nucleus; meaning the charge, the negative charge can be much better stabilized because you are much closer to the nucleus.

Whereas, in the case of $sp^2$ hybridization, now the s character, the percentage of s character has decreased; so, what you have is a lesser stability for that negative charge. As a result of which this particular compound acetylene will be more acidic and in fact, that is what you see the pKa of acetylene is close to 25 where as that for ethene in our worksheet is about 40, right. So, that's the difference in the acidities of the two compounds that arises because of the hybridization of carbon atom, okay.

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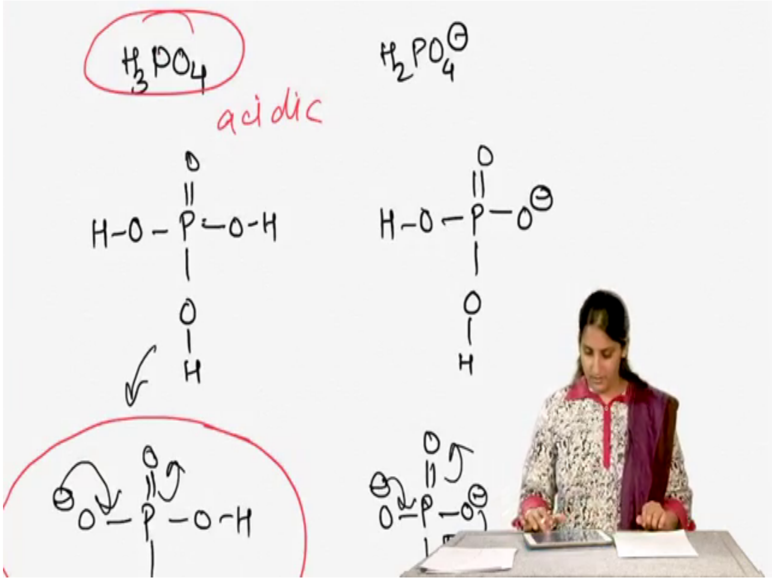

Let's go to the next question; the next question talks about $H_3PO_4$ versus $H_2PO_4^-$, right. So, let us again draw the $H_3PO_4$ structure versus $H_2PO_4^-$, right. Now, if you really see the second one this $H_2PO_4^-$ is the conjugate base of the first one; whenever that is the case you can pretty much assume that the initial acid is much more acidic, right. That is because now as this molecule loses a proton and the conjugate base of this molecule will look like this, where as in this case it will look like this, right.

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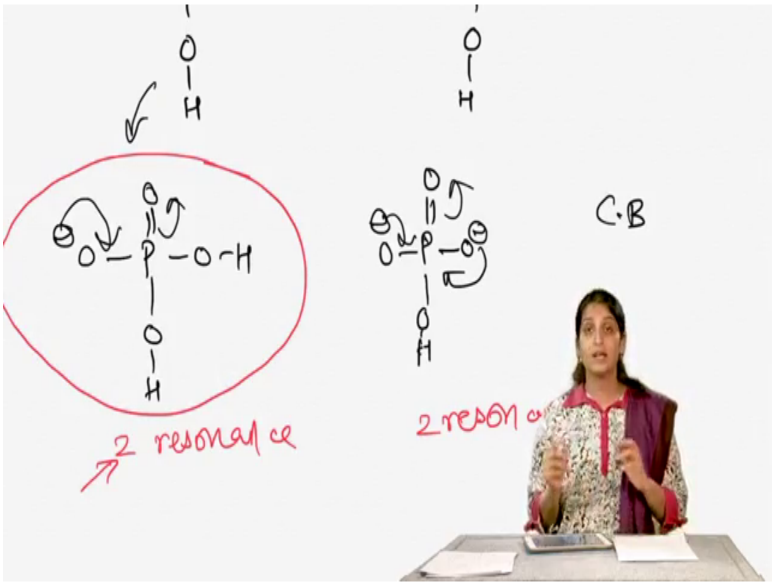

If you see the possible number of resonance structures I can resonate this charge like this, where as in this case you have two of the oxygens putting electrons really making this particular compound much more unstable, right. So, the conjugate base in this case has a much better stability right because you can draw that resonance contributor much better.

Whereas even though there are two resonance structures here and two resonance structures here, in this case there is one unit of negative charge that has to be stabilized; whereas, in this case there are two units of negative charge that has to be stabilized hence $H_3PO_4$ becomes a much more acidic molecule because its conjugate base is much more stable; okay.

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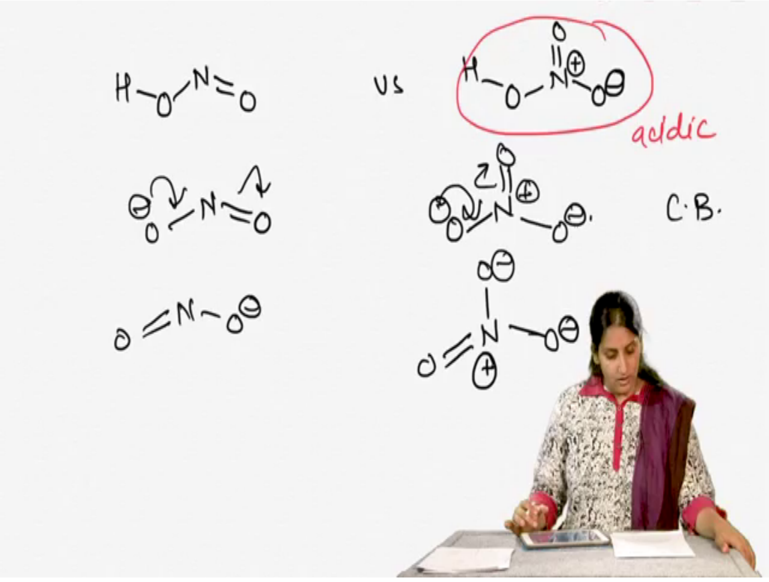

Let’s move to the next one; the next question talks about $HNO_2$ versus $HNO_3$; right, okay. Again draw the conjugate base. Whenever you are faced with what is the acidity of two molecules and if you have to compare them, first thing we do always is that we draw their conjugate bases and we check the acidity of the conjugate base, right. Now, in this case if you really see I have a pair of resonance structure that looks like this where as in the other case I have also resonance structure that looks like this.

But in this case you have a positively charged nitrogen atom that is much more inductively electron withdrawing and can really stabilize the negative charge. So, $HNO_3$ becomes much more acidic as compared to $HNO_2$ okay; let’s go further.

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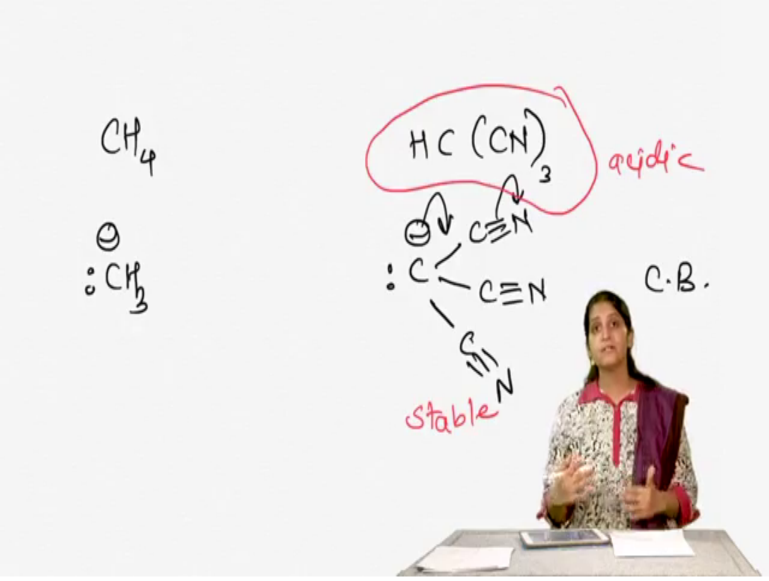

Now, I have a question between $CH_4$ and $CH\ (CN)_3$, right. Now, let us think about it; again draw the conjugate bases for the corresponding acid; this will be $CH_3^-$ whereas, this will be, instead of Hydrogen now you have a cyano group.

If you really think about it each one of these cyano groups has the structure like this. So, if I draw it completely it looks like this; right; and the negative charge on that carbon is now much more stabilized because you can push electrons here and each one of those cyano groups can undergo resonance structure and give you a possible resonance contributor. Also remember that the cyano, C≡N is an inductively withdrawing group. So, it’s gonna pull electron towards itself. So, what happens is as a result of this; this becomes much more stable. So, if the conjugate base is much more stable the corresponding acid becomes much more acidic. So, in this case this will be our acidic molecule, okay.

So, remember whenever you are asked to compare between two molecules, we are not asking you to compare two random molecules; there has to be some comparison possible between the two molecules and always look for that comparison point, in the sense, is the element the same or if it's a different element then what is the difference in their electronegativity; what is the difference in their size, right or if it is the same element, then is the hybridization same; is the number of resonance structures the same? So, whenever possible look for that point of difference between the stability of the conjugate bases of two compounds.

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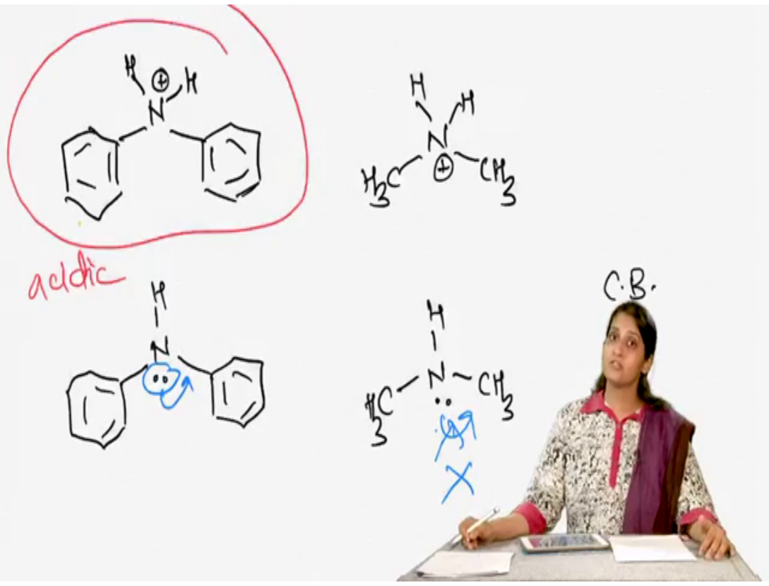

I am gonna look at one more compound here; this is a little tricky one; in this case both of them look like they are the corresponding protonated amines, right. Now, the question is which one amongst them is really much more acidic, right. Let's look at the conjugate bases. Now, in the first go both of the conjugate bases look really stable because you have given rise to two neutral molecules; they do not have charges; the conjugate base looks much more stable in each case, right.

So, then what we do is we look further right we want to make sure one of them has to be a little more stable than the other. If you think about this first one, the lone pair on the Nitrogen can now really resonate into both rings right; it can spread over the two rings because you are now able to push these two electrons into each one of the rings and give rise to much more number of or many more resonance structures in this case.

Whereas in the other case this Nitrogen cannot really push electrons towards that carbon that kind of resonance structure is not possible. So, what we have here is, this particular molecule is much more acidic because the corresponding conjugate base allows that nitrogen to push its electrons into the ring system and make it much more stable, okay. Let's go to the last question in this series.

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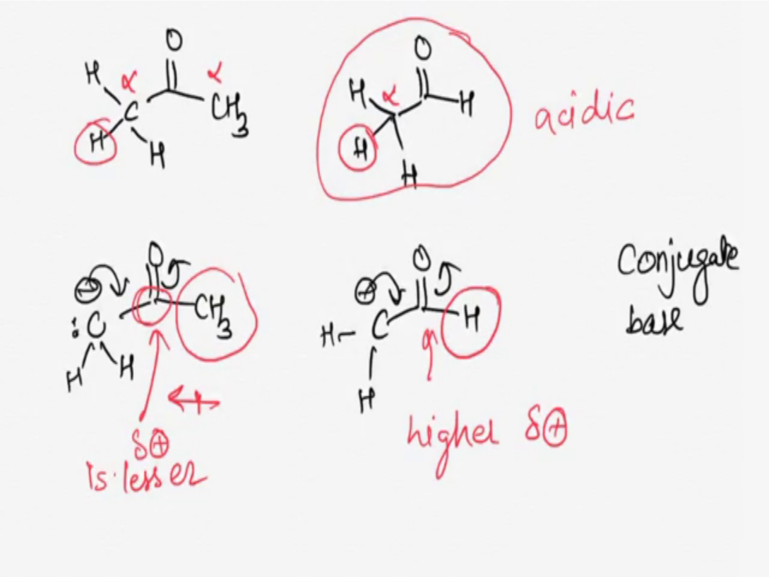

Now, the next question we have is between a ketone versus an aldehyde and what we are comparing is the alpha hydrogen right or the acidity of alpha hydrogen. So, one of these hydrogens, alpha hydrogen meaning the hydrogen on the carbon that is one carbon away from the C=O or the next carbon that is attached to the C=O; what is the acidity on that carbon?

So, in this case, this is an alpha carbon, this is an alpha carbon, this is an alpha carbon right, okay. So, now, what we are going to do is again the first step is looking at the conjugate base. And what do we have? The conjugate base in this case looks like this; here the conjugate base looks like this.

Now, if you think about it, both of them are carbons right; the negative charge is beared on both the carbons; you cannot really compare the element that bears the negative charge. So, you go further you look for resonance structures. If you really see both the molecules have equal number of resonance structures because I can create a resonance structure by pushing electrons towards that carbonyl carbon which is the same case in both the cases. So, you really cannot till now differentiate between the two molecules just based on number of resonance structures.

But then when you think about it, the point of difference in the molecule comes between this ketone and this Hydrogen, right; so, ketone and aldehyde; the $CH_3$ and the Hydrogen. The $CH_3$ group here is inductively electron donating all alkyl groups push electrons into the sigma bond because they are inductively electron donating whereas, the Hydrogen is not inductively electron donating.

As a result of which what happens is that the positive charge, the delta positive that is on the carbon reduces in the case of a ketone. What happens is, the ketone, that delta positive or the partial positive on the carbonyl carbon is not as strong as in the case of an aldehyde. As a result of which the resonance contributor will be less, right because this negative charge is not getting stabilized by the delta positive more, right. So, this is delta positive is lesser; and there is much higher delta positive here.

As a result of which we have this particular aldehyde being much more acidic because this particular negative charge is being stabilized by that higher delta positive on the carbonyl carbon making the compound much more stable. So, the conjugate base in the case of aldehyde is much more stable than that of the ketone, okay.

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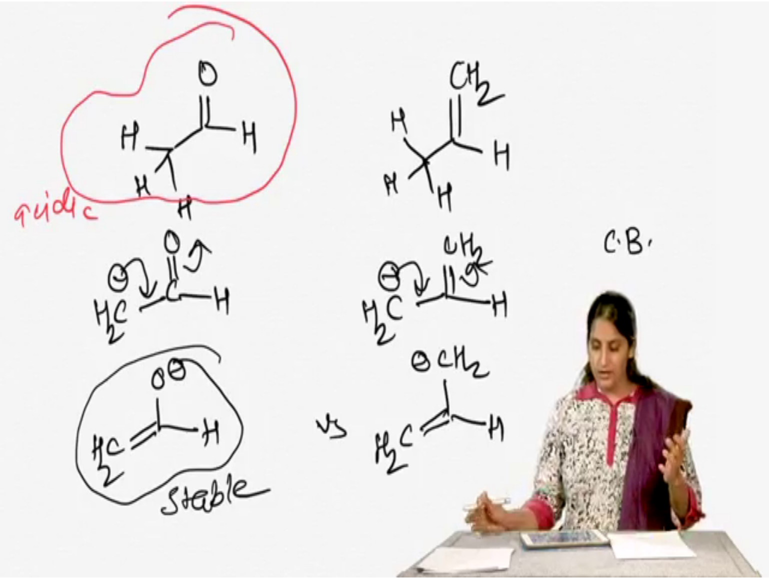

Let’s go to our last example; this one is, let’s do one more; this is; right. So, in each case let us look at the pKa of the corresponding proton, what we have to do is we have to look at the conjugate base in each case $CH_2^-$ HC=O versus $CH_2^-$ HC=$CH_2$.

Now, let us compare; I have to look at the stability of these two molecules. In both the cases the charge is on carbon, so we really cannot compare the element; but if I really compare now if I compare the resonance structures let us draw the corresponding resonance structures, what you will observe is that in this particular first compound one of the resonance structure has an oxygen that bears the negative charge; whereas in the other case in both the resonance structure there is a carbon that bears a negative charge.

So, what you have seen here is that the oxygen versus the carbon that bears the negative charge, you obviously know that the oxygen can hold on to that negative charge much more effectively than the carbon, right. So, in this case this one this particular resonance structure is much more stable; whereas in this case both the resonance structures are equally stable or unstable you want to call it, but in the first case you have given rise to one of the resonance contributors being much more stable. As a result of which the corresponding starting material is much more acidic, okay. Let’s go ahead and let’s look at the next question.

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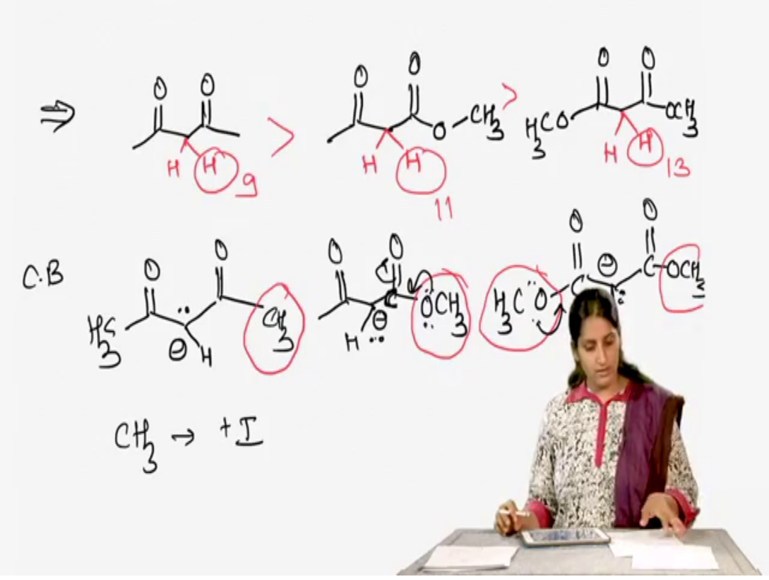

So, the next question talks about, arrange the molecules based on increasing acidities. The first molecule is a diketone the next molecule is a beta keto ester and the next molecule is beta diester molecule right, okay . Again if we have to look at the acidity we first need to figure out which is that proton that is the most acidic in each case; okay. If you think about it in each of the cases we have these protons in the middle which are really acidic in nature.

Now, why am I saying that? Because if you create the negative charge on that carbon by removing that proton then that negative charge can be stabilized such that it can be spread on two carbonyl groups which are adjacent to it, which really makes the negative charge much more stable and hence that particular proton much more acidic. So, now, let us draw the conjugate base in each case; okay.

So, now, let us look at these three things, if you look at each one of these conjugate bases and if you want to predict the stability. Remember that each one of them are going to have equal number of resonance structures because in each case you have a C=O right adjacent to it; right; or rather on both the sides of it. So, the negative charge can be spread on either of the C=O rather on both the C=O's to make it much more uniform and stable.

Then what is the point of difference? If you really see the point of difference that really comes here, you have a $CH_3$ group in each case. So, the difference, point of difference is this; $CH_3$ versus $OCH_3$ and in the last one there is an $OCH_3$ on both the side, so that is really the point of difference. So, how is this $CH_3$ versus $OCH_3$ versus both $OCH_3$ is really making a difference, right.

We have seen that methyl groups are inductively electron donating, right. So, $CH_3$ is going to give you electrons into the system making it unstable. What about $OCH_3$? That Oxygen is pulling electrons away, right; so, that is one thing to think about is that, that Oxygen is inductively electron withdrawing, but think about it; Oxygens can also donate electrons via resonance.

So, one of the things is you can have this resonance structure or you can have this resonance structure. In fact, that is what you observe and the resonance effect really takes over the inductive effect. So, what happens is that the oxygen can push electrons into that C=O making that oxygen here, the carbonyl carbon and oxygen bond really rich in electrons, as a result of which the negative charge really doesn't get stabilized.

So, what happens is if you really see the pKa of these compounds, this particular proton here has a pKa close to 9; this particular compound here has a pKa close to 11 and the next one will have a pKa close to 13. As a result of which you can see which one is much more acidic, the diketone is much more acidic than the ester and which is much more acidic than the corresponding diester molecule; okay.

Let's go ahead and let's look at one more question, okay. So, now, the question is, in the following compounds which hydrogens can be removed faster by the base and why? Right. So, which one or rather the question is, which hydrogens are much more acidic? Right.

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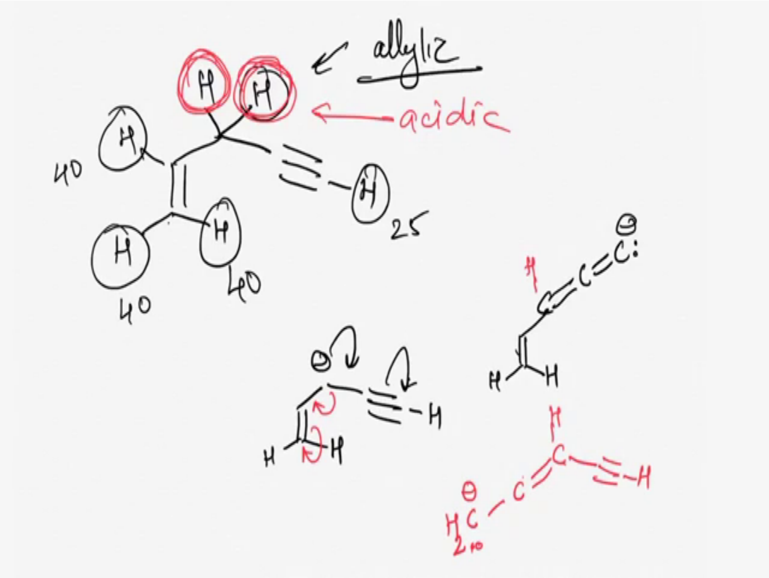

So, let’s look at the first molecule here. One of the ways to think about it is we can go ahead and really look at the pKa’s of each of these types of protons. So, if you think about it this is pKa around 25 right because it’s on sp hybridized carbon, this is about pKa 40; this one is also about pKa 40 okay; this one is also about pKa 40; right. On the first looks, it looks like this one here will, being on an $sp^3$ hybridized carbon could be about pKa 60, but that’s not the case right. Why?

Because if I create a negative charge on that carbon in the conjugate base that negative charge can be spread on either of the 2 carbons; one on this side and one on the other side and I can really give rise to multiple number of resonance structures if that happens. So, this is an allylic position and we will look at what allylic positions are in alkenes, but to go over it, allylic positions are the carbons next to a double bond or a triple bond, right.

Whenever you have an allylic position that carbon can be much more acidic because now when you create a negative charge on that carbon or a conjugate base on that carbon that negative charge can be stabilized by resonance on either side. So, if I draw the corresponding conjugate base, this can be spread by a drawing resonance structure here or you can also spread this such that you can draw the resonance structure on the other end. So, I can draw one resonance structure on this side as well, right.

So, when I look at these, any of these protons they are much more acidic in the entire molecule and if I put this molecule in base that is the proton that will be first removed in an acid base reaction; okay.

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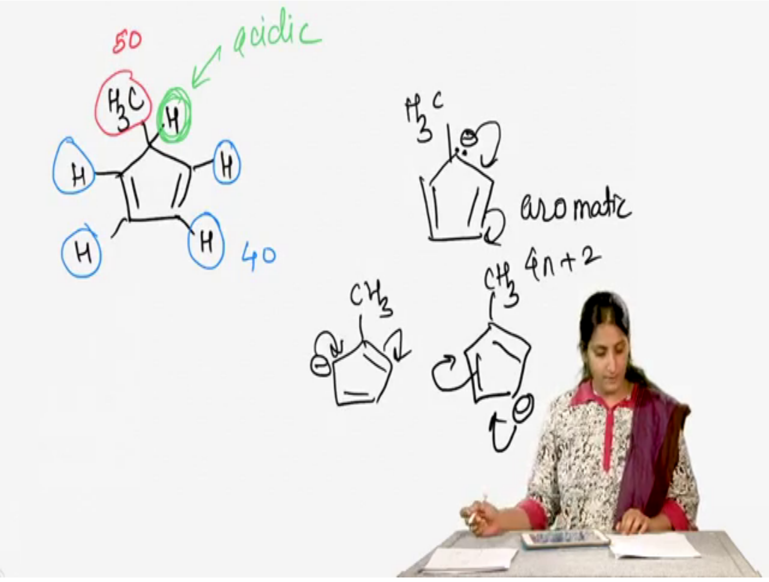

Now, let us look at the next one; the next one is here; okay. Now, as we look at all the protons in the molecule let's think about it, these are all vinylic protons meaning they are on the carbon-carbon double bond; their pKa is about 40.

Let us look at this one here, this is such that it is not allylic; allylic is only one carbon away from the double bond this is two carbons away. So, this is more like an $sp^3$ hybridized carbon. So, this has a pKa close to 50 to 60, so let's call it pKa 50. But if you look at this one proton here; okay, if I deprotonate the, that one proton and make the corresponding conjugate base, what do I give rise to? I give rise to this particular anion.

Now, this carbanion is extremely stable. Why is it extremely stable? If you recall the aromaticity example that we did in class this particular anion the cyclopentadiene anion is one of the most stable anions because it is aromatic in nature, okay. Think about it, it has planar; it is planar, it has (4n + 2) pi electrons in there; so, total 6 electrons. It also can resonate right such that it can really give rise to so many resonance structures, right. So, you can give rise to so many resonance structures and really make this particular carbanion much more stable, okay.

One key things to look at here is that the carbon that bears that negative charge is not really $sp^3$ hybridized, it is $sp^2$ hybridized. Why is it $sp^2$ hybridized? Because if it is $sp^2$ hybridized; that means, that it can put that lone pair of electrons into the p-orbital. The p-orbital that does not take part in hybridization and that lone pair of electrons can be shared over all the other carbons in conjugation making the (4n + 2) pi electrons, which in turn makes the molecule aromatic, which in turns gives it much more stability; right. So, the most acidic proton in this case is this green one.

So, the next question is, arrange the following compounds in the increasing order of pKa's. Again what we have to really think about is what is the acidity of each compound, right.

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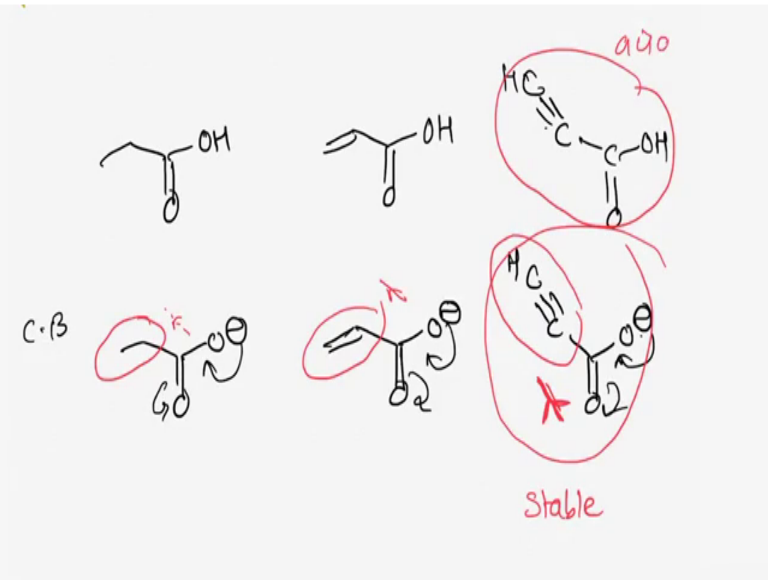

So, let's look at the first one; then you have a double bond instead of a single bonded Carbon and then you have a triple bonded carbon adjacent to that COOH, right. So, these are the compounds. Again we look at the most acidic proton which is gonna be in this case the C=OOH, the carboxylic acid proton and the first thing we do is we draw its conjugate base. So, what do we have here? Okay so, we have the corresponding conjugate bases.

Now, to think about the stability of the conjugate base again first start from the element that bears the negative charge, it is oxygen in all three cases. So, we really cannot differentiate based on the element that bears the negative charge; we then look at the corresponding resonance structures. If you think all three of them have the same number of resonance structures because really I can draw resonance structures like this for each one of them right; okay. So, I really cannot differentiate it based on the number of resonance structures as well, then I look for inductive effect.

So, the inductive effect in this case is gonna be by these groups. So, in one case you have a CH $_2$CH$_3$ group, in the other case you have a CHCH$_2$ group and in the other case you have a

CCH group which is really the triple bonded group, right. If you think about it, the triple bonded carbon or the sp hybridized carbon is really electronegative in nature; it wants to pull electrons away, close to itself, because there is much higher s character to that Carbon.

As a result of which the negative charge is pulled much effectively towards this side as compared to that here and there is really lesser of a pull here, right, which makes this corresponding conjugate base much more stable and the corresponding acid much more acidic.

Okay, so, which in turns make this corresponding conjugate base much more stable, which makes the initial molecule much more acidic. So, the acidity order has to be such that this one is much more acidic as compared to the second one and the second one is much more acidic as compared to the first one. This is gonna be the trend because sp hybridized carbon is much more electron withdrawing inductively as compared to $sp^2$ and $sp^2$ is much more electron withdrawing as compared to $sp^3$; okay.

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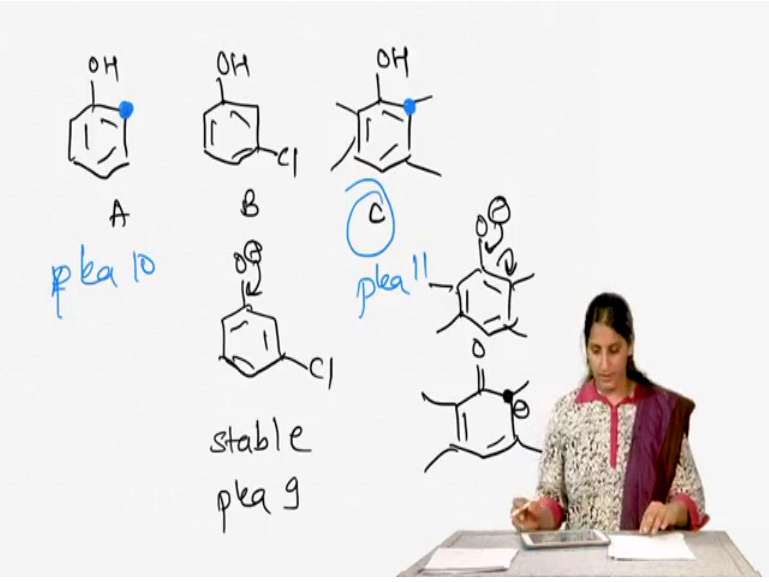

So, now let us look at the next one; the question is Phenol shown below have pKa values of 9, 10 and 11 and the question is which one is which? Right so, A B and C, three phenols are given to you; right and the question is 9, 10 and 11, which one is which? Now, if you really see the phenol that is gonna be most acidic; the highest acidity is the, going to be the one with the Chlorine on it. Because in each case really what you have is you are gonna form phenoxide ion as the corresponding conjugate base.

In this case this particular phenoxide ion will be more stabilized because resonance structures also possible, but remember that chlorine is pulling electrons inductively. So, this is much more stable. So, this one will be our pKa 9, much more acidic corresponding molecule. Now, between A and C, let's look at the corresponding conjugate base of C; if I draw this resonance structure, if you see this carbon here that bears the negative charge right, this particular carbon.

Now, that carbon is not as stable because what happens is there is going to be an inductively electron donation by that methyl group, right. So, this one is gonna be much more unstable as compared to this carbon. So, if I compare the carbon here, the blue carbon here versus the blue carbon here, when they have a negative charge on them. The one in this case for C is gonna be less stable because it has also the electrons coming from the methyl group, the inductively donating methyl group that is making it unstable. As a result of which you have C being much less acidic as compared to A so, this one will be pKa 10 and this one will be pKa 11, okay. So, that is the case.

Now, let us go to our last questions; last set of questions, and the last set of question really ask you to draw an equilibrium reaction and they ask you to figure out the Keq of the reaction, right.

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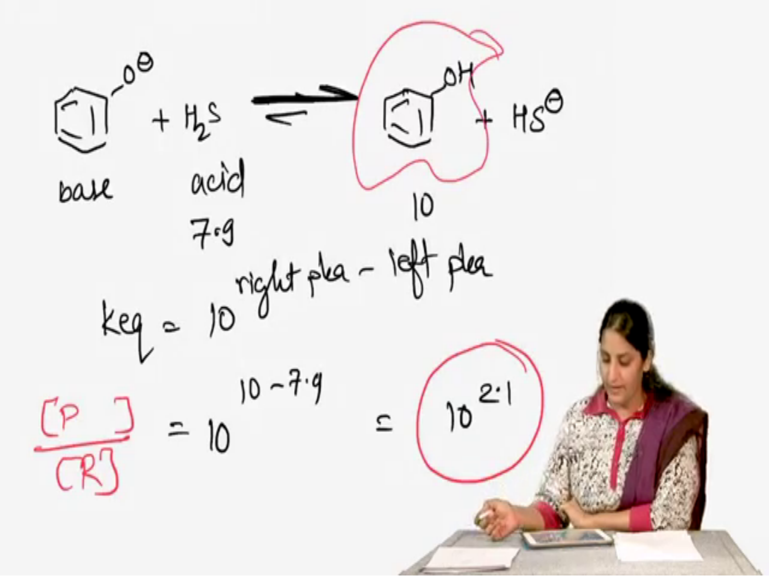

Let's do the first one it is a reaction between phenoxide and $H_2S$. So, phenoxide and $H_2S$; whenever you are faced with such a question please the first thing you want to do is make sure that you know which one is the acid and which one is the conjugate acid.

In this case phenoxide is gonna be our base $H_2S$ is going to be our acid; the conjugate acid is going to be phenol and the corresponding conjugate base is gonna be a $SH^-$. Now, the pKa of $H_2S$ is given as 7.9, we know from our pKa table that the pKa of phenol is about 10, right. So, what is gonna be the case? So, the Keq is gonna be,

$$Keq = 10^{\text{right pKa} - \text{left pKa}}$$

So, that is,

$$Keq = 10^{10 - 7.9}$$

That is,

$$Keq = 10^{2.1}$$

That really means that the equilibrium is drawn towards phenol, right; as a result of which your Keq is much more positive; Keq let me remind you again it is the concentration of products over concentration of reactants, right. So, there is much more phenol into the system than $H_2S$; let's go further.

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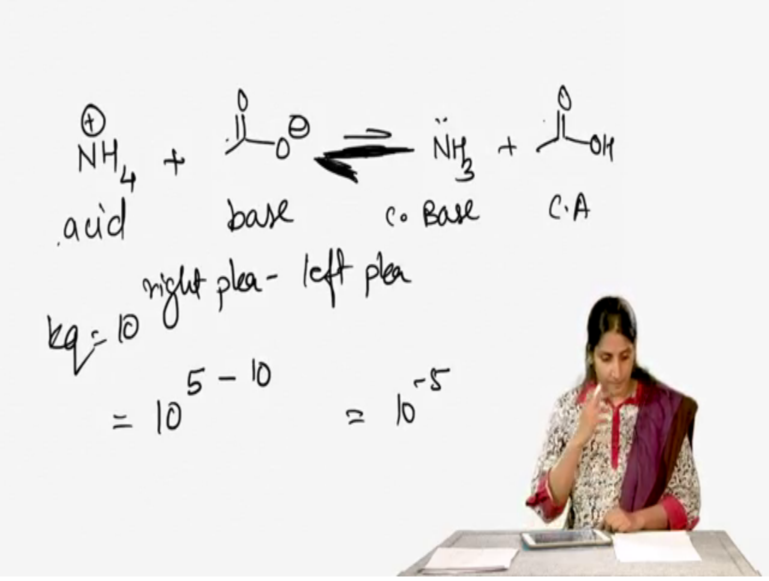

Now, we have one more question it is a question of what is the Keq for the reaction between $NH_4^+$, that is the ammonium ion and acetate ion, right. Again this is going to be my acid, this is going to be my base, this will be my base and the corresponding conjugate acid is gonna be acetic acid, right. Now, the Keq again will be

$$Keq = 10^{\text{right pKa} - \text{left pKa}}$$

So, that becomes 10 to the power right pKa, which is 5, minus the left pKa, which is ammonium ion which is 10.

$$Keq = 10^{5-10}$$

So, this will be,

$$Keq = 10^{-5}$$

Which means that the products are really-really less in numbers. So, an acetate ion really cannot deprotonate an ammonium ion; and the Keq, or the reaction is really driven such that it is driven towards the reactants and not towards the products.

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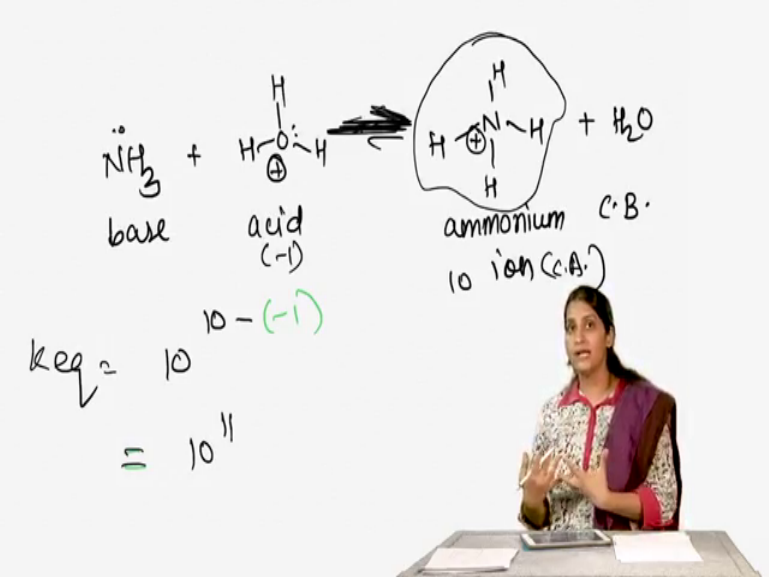

Let's do one more question. Now, the question is between ammonia and $H_3O^+$; right and again this is gonna be my base; this is gonna be my acid and, what do we form here? We form an ammonium ion and then we form water as our conjugate base, right. Now, if you look at your Keq which is 10 to the power right pKa; so, 10 to the power 10 right; this is my conjugate acid, 10; this is minus 1 on the other side. So,

$$Keq = 10^{10-(-1)}$$

$$Keq = 10^{11}$$

Meaning if I mix the hydronium ion and if I mix ammonia together I will quickly form this, right, in huge quantity because that is really the concentration of my products. So, which is 10 to the power 11 as compared to my concentration of reactants which is 1, right. So, acid-base reactions really give us a way to predict if two molecules are mixed into the flask, what really happens? Does it mean that both of them are gonna quickly react; both of them are going to tremendously react to form the products or will they just sit around? Right.

So, in the first case for example when we looked at the first reaction we form the phenol in excess, right, which meant that the reaction is gonna go forward; whereas, in the second case when we were looking at, acetate really did not react with ammonium ions. So, which meant that if I mix these two ions together, pretty much nothing will happen; they will sit around in the flask just like two separate ions, right; they are not gonna react together.

So, that’s why acids and bases or the mastery over acids and bases is really important because it gives us a clue as to if I react two compounds together will they really react or will they just avoid reaction and just sit idle, right. So, that’s why make sure that you are mastering your acids and bases because they are going to play a huge role in predicting the reactivity of the molecules as we go ahead, okay.

Thank you.