Introductory Organic Chemistry
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Lecture - 20
Acids and Bases
Part-2

In the last class we looked at the pKa table and we also said that we will use this pKa table to figure out the outcomes of Organic Chemistry Reactions right. So now, what we are going to do is we are going to use the pKa table to first predict the K equilibrium of any acid base reaction.

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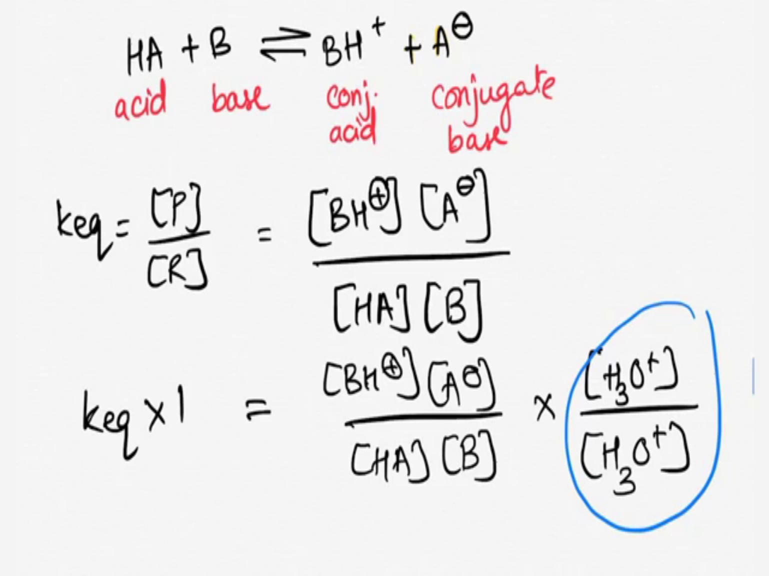

$$HA + B \rightleftharpoons BH^{+} + A^{\ominus}$$

acid base conj. acid conjugate base

$$keq = \frac{[P]}{[R]} = \frac{[BH^{\oplus}][A^{\ominus}]}{[HA][B]}$$

$$keq \times 1 = \frac{[BH^{\oplus}][A^{\ominus}]}{[HA][B]} \times \frac{[H_3O^+]}{[H_3O^+]}$$

So now, let us take a generic reaction I am going to take,

$$HA + B \rightleftharpoons BH^{+} + A^{-}$$

So, this is a generic acid-base reaction. Now, just to make you guys go back we talked HA being the acid, because it gives us a proton; B is the base, BH^+ which is going to act as a conjugate acid right, because if the reaction has to go back it needs to function as an acid. So, I am going to say conjugate acid and A^- which is going to function as the conjugate base, right.

So, this is a generic reaction between acids and base to give you conjugate acid and conjugate bases. Now, the K equilibrium (Keq) of this reaction we have said is equal to concentration of products over concentration of reactants, right. So, concentration of products; so in the case of products, I have

$$Keq = \frac{[P]}{[R]} = \frac{[BH^+]\,[A^-]}{[HA]\,[B]}$$

Now, let us explore this equation little further, what I am going to do is I am going to multiply this Keq by 1, okay.

So, I am going to write Keq into 1 is equal to concentration of BH^+ concentration of A^- over concentration of HA and concentration of base. Now, on the left hand side we multiplied by 1, on the right hand side also we are gonna multiply by 1, but we are going to multiply it in this notation. So, we are multiplying and dividing by H_3O^+, so this term in all is 1, right. So, we are multiplying both sides by 1.

$$Keq \times 1 = \frac{[BH^+]\,[A^-]}{[HA]\,[B]} \times \frac{[H_3O^+]}{[H_3O^+]}$$

Now let us separate these terms a little bit.

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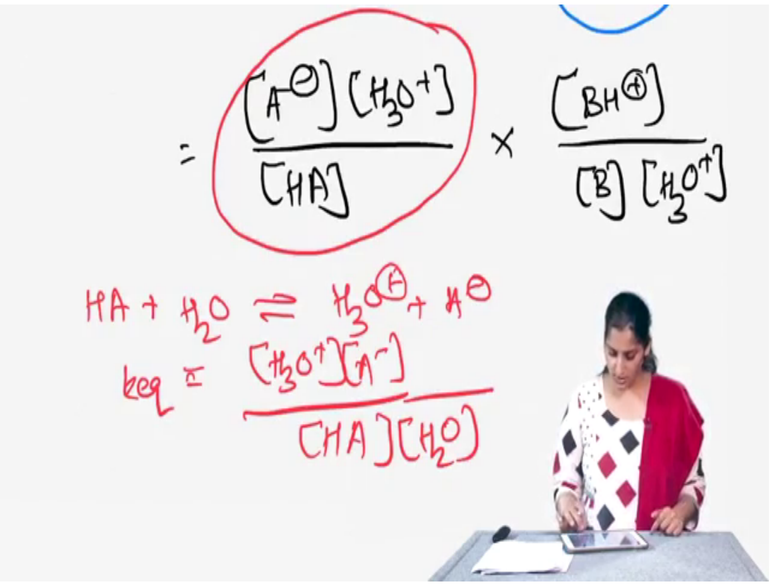

So, what I have here is,

$$Keq \times 1 = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[BH^+]}{[B][H_3O^+]}$$

So, I have not done anything different, but I have just written these term such that I have separated, such that they make some sense. Now, if you would look at this particular term what does it remind you of? If you look closely this particular term talks about the Ka of dissociation of an acid HA. How is that? Let us look at that.

So, if I take

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

wherein water acts as a base.

And what will be the Ka of this particular reaction? So, Ka would be

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

Rather if you want to go back and revise something that we saw in last class, Keq will be concentration of products over concentration of reactants so that is it.

$$Keq = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

But when we multiply Keq by concentration of water which is pretty much constant during the reaction we get Ka.

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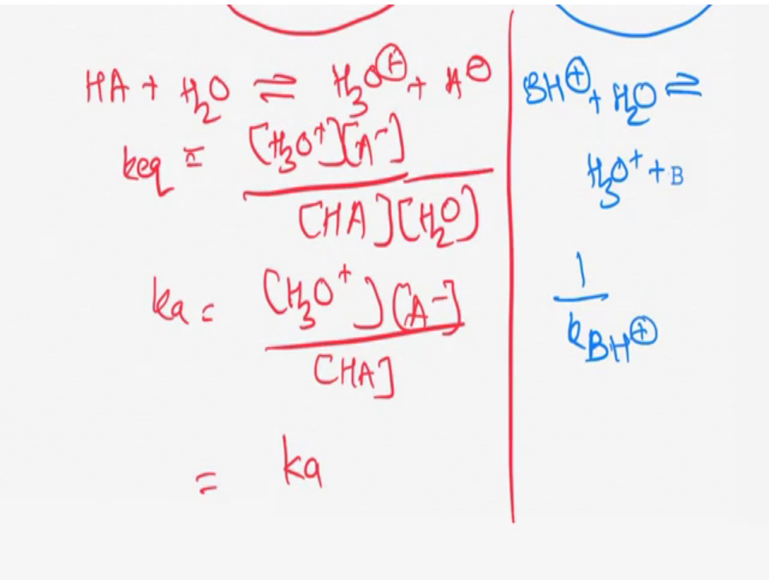

So, Ka will be

$$Ka = Keq\,[H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

So, this is Ka. This particular other term on the other side is actually the dissociation constant for an acid BH^+, so which is exactly the same. So, I will not go through the details, but you can see BH^+ plus H_2O and you can figure it out yourself giving you H_3O^+ plus B.

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$$

So, this particular term here

$$\frac{[BH^+]}{[B]\,[H_3O^+]}$$

will be $1/K_{BH^+}$.

$$\text{Since } K_{BH^+} = Keq\,[H_2O] = \frac{[H_3O^+]\,[B]}{[BH^+]}$$

So, our initial reaction which was HA plus B giving you A^- plus BH^+ and the Keq for that.

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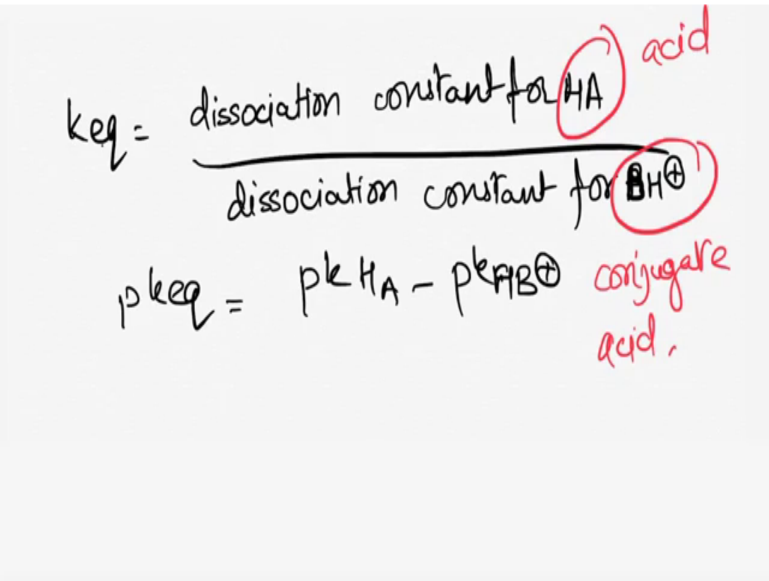

$$keq = \frac{\text{dissociation constant for } \boxed{HA}}{\text{dissociation constant for } \boxed{BH^{\oplus}}}$$

acid

$$pkeq = pk_{HA} - pk_{HB^{\oplus}}$$

conjugate acid.

So, the Keq for that is nothing but

$$Keq = \frac{\text{Dissociation constant for HA}}{\text{Dissociation constant for } BH^+}$$

Now, let us take the pKa. So, pKeq will be

$$pKeq = pK_{HA} - pK_{HB+}$$

I want to point out one thing HA was our acid and BH^+ was our conjugate acid as we started writing this reaction, right. So, what I have here is Keq will be dissociation constant for the acid divided by the dissociation constant for the conjugate acid, right in any acid-base reaction.

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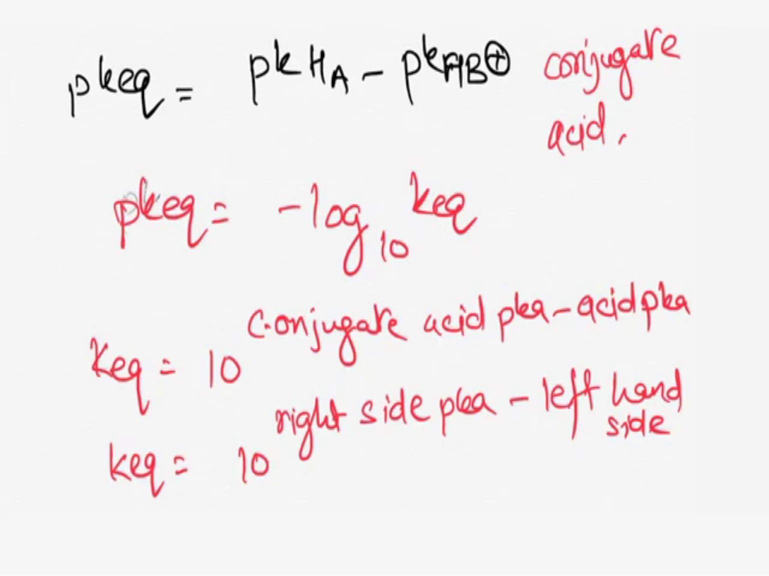

$pkeq = pk_{HA} - pk_{HB^{\oplus}}$ conjugate acid.

$pkeq = -\log_{10} keq$

$Keq = 10^{\text{Conjugate acid pka} - \text{acid pka}}$

$keq = 10^{\text{right side pka} - \text{left hand side}}$

So, if I have to generalize, if I take the negative anti log of this particular reaction right, because pKeq will be,

$$pKeq = -\log_{10} Keq$$

So now, if we take the antilog then what I have is, Keq will be,

$$Keq = 10^{\text{conjugate acid pKa} - \text{acid pKa}}$$

So now, we have this formula or if you want to simply remember Keq will be,

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

And, this is a very useful equation because with this equation I can figure out the Keq of any reaction right. So, now let us look at couple of reactions of acids and bases. So, I am going to take a reaction here which is acetic acid and water right.

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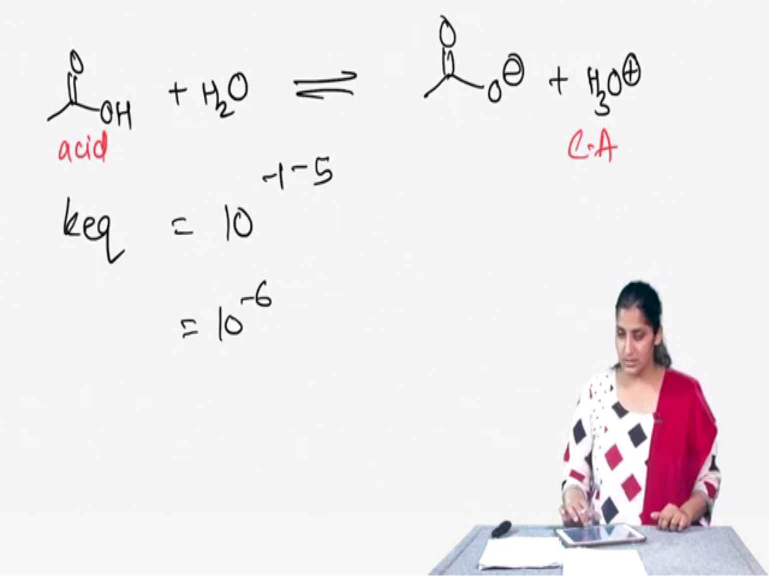

Now as these two molecules react you are going to form acetate and H_3O^+, right. Let us figure out the Keq for this particular reaction using the formula that we just derived. So, the Keq for this reaction, first I need to figure out the acid and the conjugate acid. The acid here the molecule that is losing the proton is actually this one which is our acetic acid and the conjugate acid which is going to lose a proton in the backward reaction is going to be the H_3O^+, right.

So, in this case Keq will be 10 to the power conjugate acid pKa which is minus 1 according to the pKa chart minus the acid pKa which is around 5, right; so that is 10 to the power minus 6. So, that tells you why acetic acid is one of the weakest acids that we see around, right or why is it termed as a weak acid as compared to most of the mineral acids HCl and H_2SO_4 or acids like that right. Because, if you see if you take 10 to the power 6 molecules only one of them probably get dissociated as we add acetic acid and water together. It's very very less dissociation happening because acetic acid will stay as acetic acid and will not form that acetate ion and thus it is termed as a weaker acid as compared to HCl, HNO_3 and acids like that, right. Now, let us look at one more reaction.

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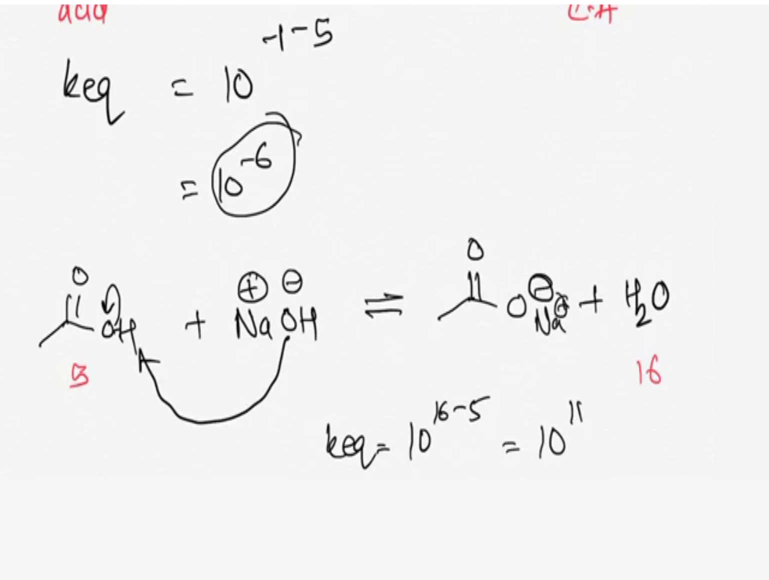

Now I am going to take acetic acid, but instead of taking water I am going to take NaOH okay. NaOH as we know is a base which is nothing but Na^+ and OH^- right. There is the ionic bond between sodium and hydroxide. So, what I have here is again this hydroxide is gonna act as a base; it's going to go and grab this proton and then push these two electrons on that oxygen. So, also pay attention to the arrow pushing because that's one of the most important things to know in an organic chemistry class.

So, the next thing is it forms water. Now let us look at the Keq for the reaction, I have acid which has a pKa of 5. I have the conjugate acid now instead of H_3O^+ the conjugate acid now is water. So, in the case of H_3O^+ you had a pKa close to minus 1, in the case of water the pKa is close to 16. So, the Keq in this case will be 10 to the power right hand side pKa which is 16 minus 5; that is 10 to the power 11, okay.

$$Keq = 10^{16-5} = 10^{11}$$

So, now you can see why acetic acid and base like NaOH will react vigorously to form that acetate ion, but the water molecule will not really dissociate acetic acid into acetate ions. So, this clearly tells me one of them has a Keq of 10 raised to power minus 6 meaning the concentration of products is very very small, right; 10 raised to power minus 6 is a very small number. Whereas, in the case of the later reaction the concentration of products over reactants is 10 to the power 11, so 10 to the power 11 it's really large number. So, you can see why acetic acid reacts with two different compounds H_2O and NaOH differently.

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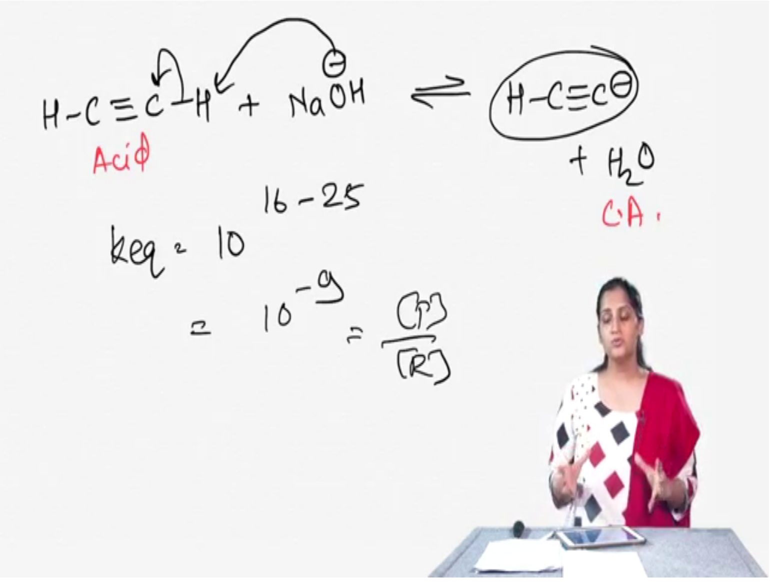

Now, let us take one more example I have an acetylene molecule and I want to use NaOH in order to deprotonate it, okay, right. Again arrow pushing, this attacks here so I have $HC\equiv C^-$ plus H_2O. Let us figure out the acids so this is the acid because it is losing the proton and this is our conjugate acid, right. Now if we take the Keq which is,

$$Keq = 10^{\text{conjugate acid pKa} - \text{acid pKa}}$$

So it will be,

$$Keq = 10^{16-25} = 10^{-9}$$

(pKa of acetylene according to your pKa chart is close to minus 25)

So, this is close to 10 to the power minus 9 right, so the Keq for this particular reaction is 10 to the power minus 9. One of the questions people ask is that since it is an equilibrium does it mean like, if I let these two compounds sit together for a long time eventually the system will reach equilibrium and such that the reactants and the products will have equal concentration. So, that’s one of the questions more often asked right. The other question that is more often asked is what about the starting concentrations of the reactants. So, like if I take a really concentrated NaOH will it eventually make the reaction go in the forward direction.

Currently understand that the Keq is 10 raised to power minus 9 which is concentration of products over reactants, again meaning that you will not form that anion that we have shown right, because concentration of the anion is very very negligible right. So, let us go back to the two questions the first question was what about the, does it mean that if I let these two sit together will it eventually lead to the equilibrium meaning 50-50 concentration.

One of the things I want to point out here is that equilibrium does not necessarily mean that a fifty percent product and a fifty percent reactant are form. We have seen such reactions before where in equilibrium meaning both the things are equal. When we assume a 50-50 distribution of concentration and products we are assuming that they are equally stable meaning the products are equally stable and the reactants are equally stable. And, then we can assume that as the reaction happens eventually it will lead to equal formation of reactants and products.

In most of the acid-base reactions you will see is that the stability of the product depends on the stability of the conjugate base that is formed. So, in this case this particular conjugate base that is formed will govern the stability of the products totally. Now what you observe is that more often in acid base reactions, the stability of the products and the reactants is not the same. As a result of which it is wrong to assume a 50-50 distribution at equilibrium; when I am talking about equilibrium let me go over the kind of equilibrium that I am referring to in the case of acid and base reaction.

Now, to give you an example of the kind of equilibrium that we are talking about I am going to use an analogy, right.

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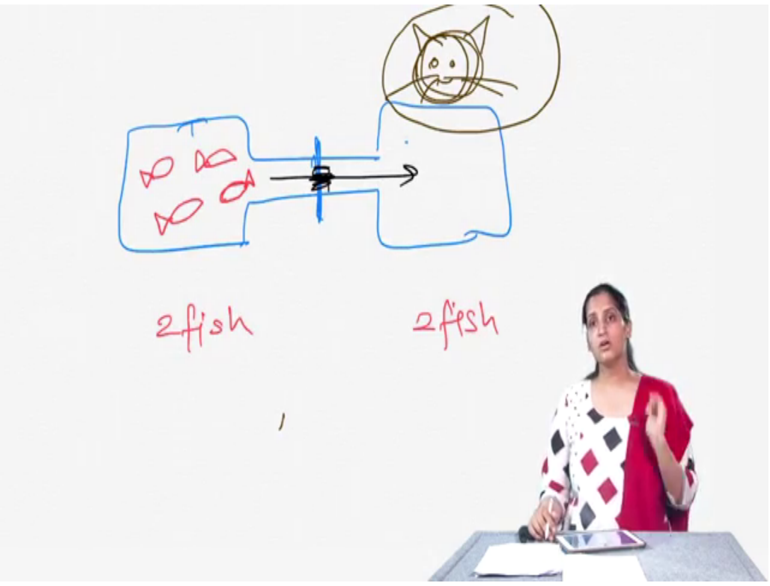

So, I am going to take a water tank on this side and another water tank on the other side, which are basically which have a gate in between right and then what we are going to do is we are going to have some fishes right. So, let's say that we start from four fish here and then at the beginning of the experiment there are no fishes on the right hand side time.

Now, as we open this gate what's going to happen eventually the fish are going to travel to the right hand side some of them will travel back and forth, back and forth. Eventually at equilibrium you may find a situation wherein there are two fish here and the other two fish are in this particular other tank. Now, again we are talking about fishes not really chemical molecules, but just imagine this as an analogy. So, the equilibrium the kind of equilibrium that we talked about previously was that 50-50 meaning two here and the other two in the other tank.

Now, imagine a situation where in you have the same fish tank, right. But now you have a cat sitting on one of the sides which is ready to eat these fishes, right. So, this particular cat, you think will the fishes will travel close to the cat? The answer would be No, right. As a result of the cat what happens is the fishes tend to be more on the left hand side than the right hand side. So, the equilibrium is skewed, meaning the stability of the products and the reactants is different because we have added some other factor right, like the cat.

So, if the new equilibrium condition is such that the left hand side tank is extremely attractive for the fishes, because there is a cat sitting on the right hand side then you will never achieve that 50-50 distribution, right. So, similar condition happens in the case of acids and bases, the stability of the end product and stability of the starting molecules really determines which side is more favored.

Now, let us look at the second question which was about the concentration of NaOH; what will happen if we use a high concentration of NaOH really really high concentration, will it be able to deprotonate? The answer is still No, okay. Now you can imagine that NaOH will react with that particular acetylene molecule, it will make that anion, but remember the backward reaction is equally favorable or rather more favorable. So, as soon as that anion is formed it's going to react with water to go back to the starting material.

So, eventually even if I wait a really long time I will never see a dominant product formation in this particular reaction, because the backward reaction is way faster than the forward reaction. As soon as the acetylide anion is formed it's going to grab the proton and go back to the starting material. So, irrespective of how much more concentrated NaOH we take we will never see that 50-50 formation here, right.

Now, one thing that I must point out is that the K equilibrium we are talking about is the ratio of final concentration of products over reactants okay; this value is dependent on the final concentration as the reaction happens what is the final concentration. But, it is independent of what concentration you started with right, it is good to understand that we are talking about thermodynamic acidities here which is the relative free energies of the reactants and products that determine the Ka values, okay. This is in contrast to the kinetic acidity where in we were just talking about the reaction rates.

So, now here in the stabilities of the products the thermodynamic stabilities of the product will also play a role in figuring out what is the Keq of the reaction, right. Now regarding the acid-base reactions, so acid-base reactions are one of the, considered one of the fastest reactions in organic chemistry. For example, for a strong nucleophile or base there is, it is very easy to abstract a proton in a deprotonation reaction than to perform a nucleophilic attack.

So, when you mix two chemicals together you are typically going to just quickly first see the acid-base reaction happening if it is possible, okay. Let us go back to our reaction here. So, NaOH was not successful in giving me a deprotonated form of the acetylene right, that is because again if you look at the Keq it was going to close to minus 9. So, if I really need to form this product which is the negatively charged ion here which base should I use. So, the answer would be I need to use a base that will give me the overall Keq for the reaction to be more than 1.

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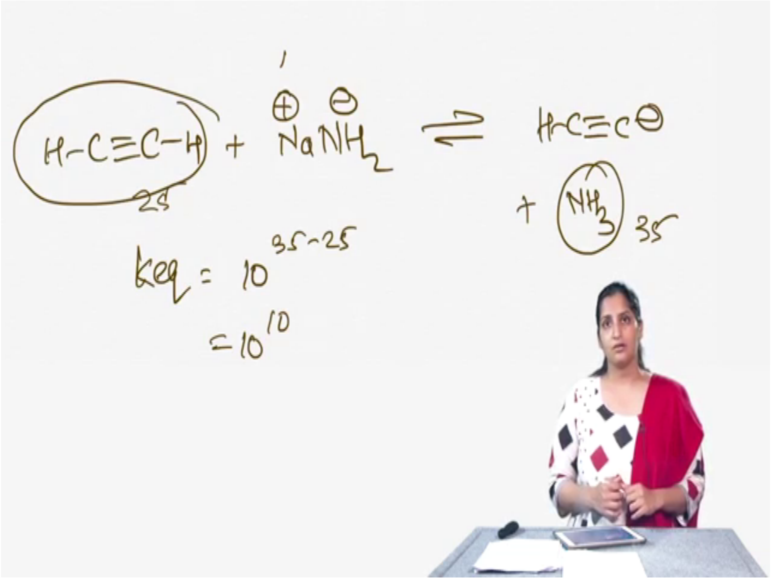

So, let us take this particular example here, I am going to take the same starting molecule and then I am going to react it with $NaNH_2$. So, instead of using NaOH we are going to use $NaNH_2$ what do I form? I form this, plus NH_3 right, because $NaNH_2$ is nothing, but Na^+ NH_2^- right. So, what do we have here if I look at the Keq for the reaction it will be,

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

$$Keq = 10^{35-25}$$

$$Keq = 10^{10}$$

So, if I use $NaNH_2$ instead of NaOH in order to deprotonate acetylene you get two different results, because in one case you are able to make the reaction go to the forward direction in the other case as the earlier one it will mainly remain as the reactant, okay. So, now, let us understand the origin of acidity. So, we can simply summarize it based on the golden rules or the 5 star principles that we had learnt in our very first class. So, what were the 5 star principles? The first one was that nature hates charges, right. So, that's something to know; any kind of charged molecule it's gonna be very very unstable and it is going to be difficult for us to stabilize that negative charge or a positive charge, right.

And, the second rule was Octet Rule rules, right. If you really think of these two rules here or the 5 star principles, they are talking about the stability of molecules right. Octet rule governs stability to the corresponding element and nature hates charges because charges are unstable so we are talking about stability. So, when we really talk about acids and bases let us write down one rule. So, the rule is stronger acids make stable conjugate bases.

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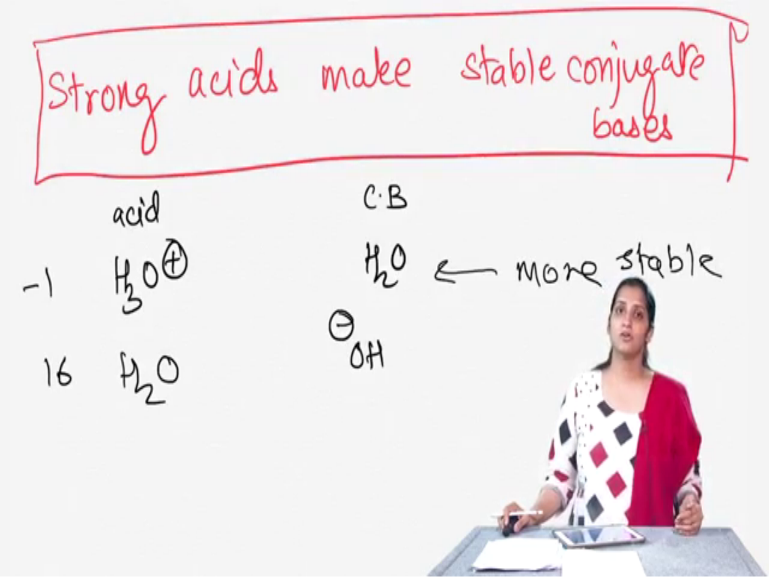

Strong acids make stable conjugate bases

acid C.B

-1 $H_3O^{\oplus}$ H_2O ← more stable

16 H_2O $^{\ominus}OH$

So, strong acids make stable conjugate bases. So, this particular rule is not a new rule it is rather as I said derived from the first two things that we have looked at. Now let us look at an example, let us take H_3O^+ right as the acid and what will be its conjugate base as H_3O^+ loses that proton the conjugate base would be water right. And now let us take water as water loses a proton the conjugate base that will be formed will be hydroxide ion right.

Let us look at the stability of water versus hydroxide ion right, water being neutral you can really find it in nature; extremely abundant form available in nature. Whereas, hydroxide ion, nature hates charges, it has a negative charge on it. So, you can easily say that this one is more stable, right. So, water is more stable as a consequence of which H_3O^+ becomes a very strong acid and that is also evident based on the pKa; so, you have minus 1 as the pKa of H_3O^+, where as 16 as the pKa of water, right.

So, you can easily say that H_3O^+ is a stronger acid because, its conjugate base that is water is much more stable as compared to water being a stronger acid. Because water's conjugate base hydroxide ion is not very stable right. One point that we need to ponder when we look at these pKa values how much stronger is the hydronium ion H_3O^+ as compared to water when it comes to acidity, right.

So, the reality is that it is 10^{16} or rather 10^{17} times stronger than water, right. So, it is not just a difference of 17 between -1 and 16; when we are really talking about acidity, remember we have to, this is pKa, we have to look at the Ka. So, it is 10^{17} times stronger acid as compared to water when we are talking about acidity.

Thus if we really wish to understand acidity, we need to understand the stability of the conjugate base. So, as we saw that nature hates charges thus we need to look at the charge stabilization; one of the things is that most of the conjugate bases are going to be charged right. So, when we are looking at a conjugate base the first question you should ask is, is the charge better stabilized in this particular conjugate base or sometimes if you have a neutral conjugate base more often that particular compound turns to be a good acid. But we will also look at those examples.

But the key question we have to always ask when we look at the stability of the conjugate base is that is there any phenomena that is making this particular conjugate base more stable.

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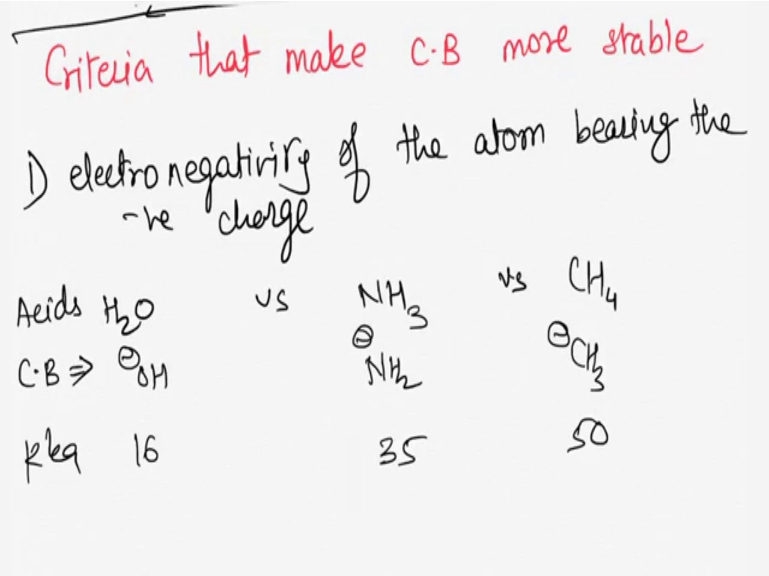

Criteria that make C·B more stable

1) electronegativity of the atom bearing the -ve charge

Acids	H_2O	vs	NH_3	vs	CH_4
C·B ⇒	$^{\ominus}OH$		$\overset{\ominus}{N}H_2$		$^{\ominus}CH_3$
pka	16		35		50

So, I am gonna go over examples and we are gonna compare two or three different types of molecules. So for example, here I have a electronegativity of the atom bearing a charge, okay. So, I am gonna go over the criterias that make the conjugate base much more stable, okay. So, or we can even call it phenomenas that make conjugate base more stable.

So, the first phenomena that we need to look at is the electronegativity of the atom bearing the negative charge, right. So, what do I have, I am going to take an example of H_2O versus ammonia versus CH_4 as acids. If all of these three were going to behave as acids what will be the conjugate bases; water will form OH^- as the conjugate base; ammonia will form NH_2^- as the conjugate base and CH_4 will form CH_3^- as the conjugate base, right.

So, the question is: what is the electronegativity of the atom bearing the negative charge, in the case of water oxygen versus nitrogen versus carbon as we move in this series. If you really think about it oxygen being more electronegative can hold on to that negative charge way better and thus it will be much more stable than the nitrogen. And nitrogen will be much more stable than the carbon because of the difference in electro negativity which is the ability of the particular element to hold on to the electrons, right.

So, in this case when we are talking about water versus ammonia versus methane, water is way better acid. So, we know that the pKa of water is close to 16, pKa of ammonia is close to 35 and for methane the pKa is close to 50, right; so that is also evident from there pKa's. But the reason, the molecular reason why water is a better acid is because, oxygen is able to hold on to the electrons way better because of electro negativity in the conjugate base. The second thing we are going to look at is the size of the atom that is holding the electrons.

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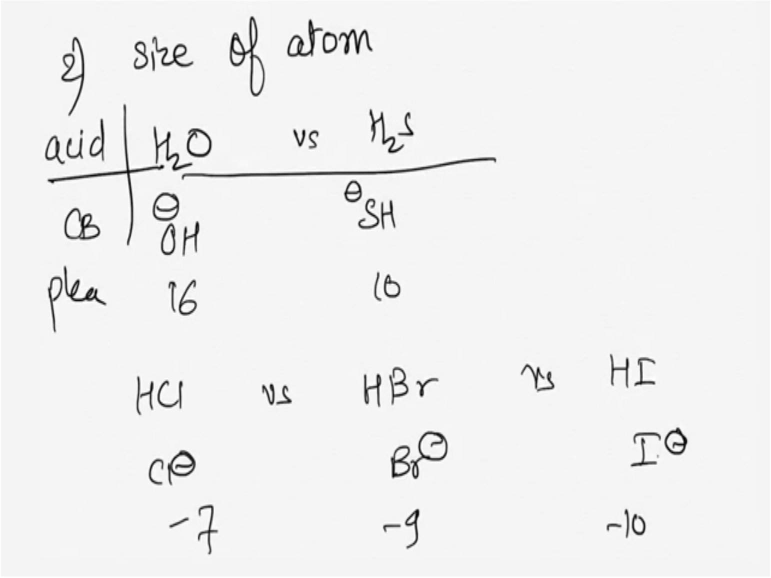

So, I am going to take an example of H_2O versus H_2S. So, water as we know will form OH^- as the conjugate base and H_2S will form SH^- as the conjugate base. Now, think of these two molecules hydroxide ion and SH^-; in the case of H_2S the conjugate base has a much larger atom that is bearing the charge, right.

So, sulfur is way bigger than oxygen. So, the negative charge can be spread on that sulfur in a much even manner as compared to being having a strong concentrated charge in the case of oxygen, right. Nature hates charges, so being able to spread that one unit of negative charge all over the big sulfur molecule, helps the H_2S to really become a better acid because the conjugate base SH^- is able to spread the charge and be more stable.

So, if you really look at the pKa here, the pKa in this case would be 16 whereas, H_2S is around 10, way better acid right. Similar phenomena is also seen in the case of HCl versus HBr versus HI. Again if you look at the conjugate base s it is Cl^- versus Br^- versus I^-, as we go down in the periodic table what happens is you have the size goes on increasing. So, I^- is really huge as compared to Cl^-, I^- is better able to stabilize that negative charge by spreading it over a large surface area. And thus HI will have a pKa close to minus 10; HBr will have close to minus 9 and HCl on the other hand will be close to minus 7 again indicating that HI is a better acid than HCl.

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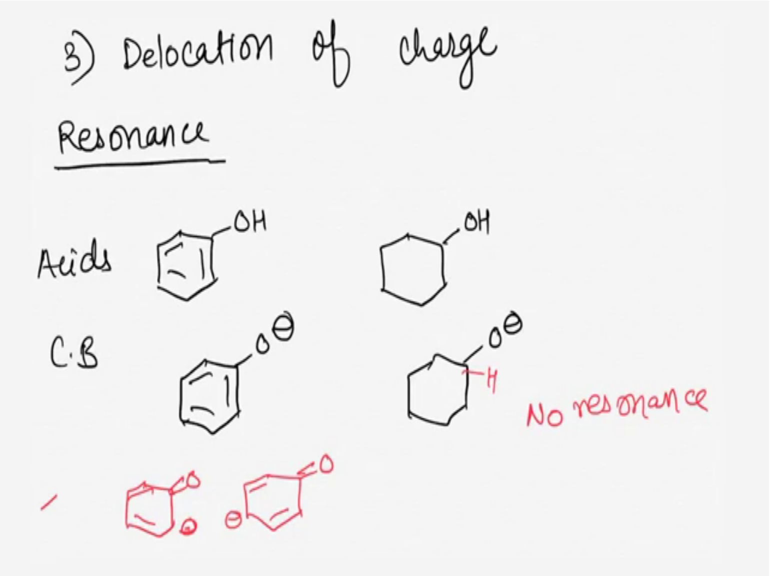

The third thing or the third criteria that we have to look at is the delocalization of charge. So, the delocalization of charge can happen in multiple ways, the first one that we are going to look at is resonance, okay. So now, let us look at an example of a Phenol versus cyclohexanol; if you look at both of these molecules both of them have very similar structure except in the cyclohexanol you are missing those double bonds. But you will see that the double bonds play a huge role in governing the acidity, right.

So, the conjugate base, so these are my acids, what will the conjugate base look like? The conjugate base here will be phenoxide ion and in this case the alkoxide ion, right. Now which one is more stable between the phenoxide and the alkoxide, if you really see that, that particular oxygen here in phenoxide can distribute the negative charge on the carbon atoms by doing a resonance structure right. So, you can spread these electrons or spread the negative charge such that you have all of these different negative structures right, so all of these are possible.

Whereas, in the case of alkoxide ion remember there are no pi bonds. So, the only bonds that you can really move in a resonance structure are the pi electrons or the lone pair electrons. Especially this particular carbon has all the four bonds sigma bonds you cannot give electrons to it right, such that there are no resonance structures here, right. In the first case there are more resonance structures, but I have only drawn two, but you can really draw up to four resonance structures.

Now, what is this resonance structure helping in? So, you can imagine that the negative charge is like a hot vessel right, I cannot hold the hot vessel all the time myself, right, effectively. As compared to if I have a couple of other people standing and I can say now you take this charge, now you take this charge kind of like that we share the burden between all of us right. This is not the exact analogy because in resonance structure what you have is a resonance hybrid. So, we have gone over what resonance hybrids are, but imagine a situation very similar where in the oxygen in phenoxide ion is able to share the load with multiple other carbon atoms the load of bearing that negative charge.

Whereas in the case of alkoxide ion that particular proton when it is lost, the oxygen has to bear the charge all on itself and is not really able to hold on to that charge very effectively right. So, delocalization helps in forming more resonance structures and more the number of resonance structures more stable is the conjugate base and as a result of which, more stronger is the acid, okay.

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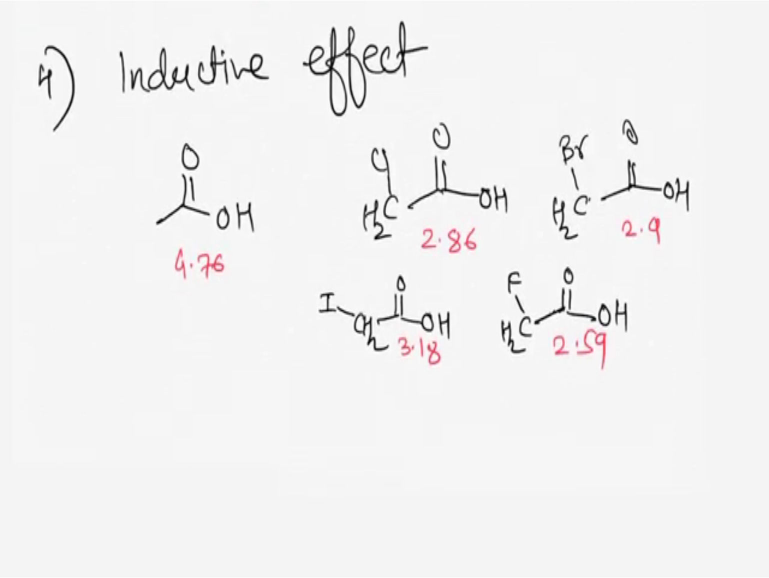

So, the fourth phenomenon that we are going to see which is very often seen is called an Inductive effect. So, in the case of inductive effect let us take two examples I have acetic acid and I have chloroacetic acid, okay. So, one of the hydrogens on that particular methyl group is now replaced with a chlorine. Okay, so now, I have Acetic acid, Chloroacetic acid I will also look at Bromoacetic acid and Fluoroacetic acid; let us also look at Iodoacetic acid, right.

Now, acetic acid had a pKa of close to 4.76 right or 5, but let us look at the exact pKa's in this particular example. Chloroacetic acid is going to have a pKa of close to 2.86, Bromoacetic acid will be close to 2.9, Fluoro is 2.59 and Iodo is 3.18. So, what does this trend really tell you?

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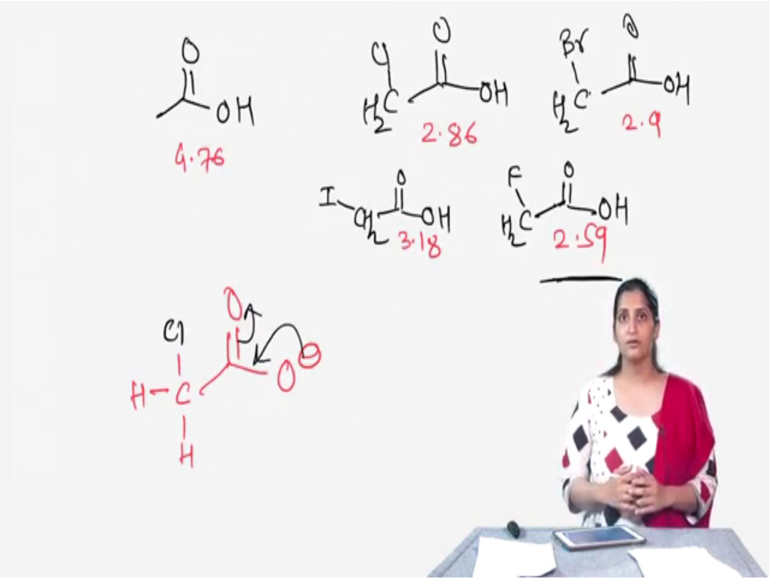

If you look at this, Fluorine is electronegative a lot more electronegative as compared to Chlorine, Chlorine is more electronegative than Bromine, Bromine is more electronegative than Iodine and Iodine is really more electronegative than that Hydrogen, right. So, as we go on adding an electronegative group at the alpha position, what we see is that the acidity goes on increasing as the electronegativity of that element goes on increasing, right.

So, if you think about it let us look at acetic acid and its conjugate base. So, in the case of acetic acid, the conjugate base is stabilized by resonance, right. Now if I change this particular Hydrogen to a Chlorine, okay, what happens is that the negative charge on that oxygen is getting of course resonance stabilized. But also chlorine being more electronegative is going to pull electrons via something called as an inductive effect.

So, Inductive effect is a through-bond effect, meaning you can pull electrons through sigma bonds and as a result of which the negative charge gets spread on the entire molecule. So in fact, you can refer to this next diagram which talks about how inductively chlorine or fluorine are being able to pull electrons away from that acetate ion, such that it spreads evenly on the entire molecule. And as a result of which what happens is you can make the acetate ion, the corresponding acetate ion way more stable, if you have any electronegative atom present.

Now, Fluorine being more electronegative pulls the electrons way better than Iodine for example. So, Fluorine makes the pKa go down to 2.59 meaning Fluoroacetic acid is going to be much more acidic than Iodoacetic acid which has a pKa of 3.18. So, all of these criterias or all of these phenomenas are very typically seen, but there are even more different phenomenas that may give rise to difference in acidity of two molecules.

We are gonna look at these phenomena in the next class and till then what you can do is you can look at the pKa chart and figure out why the pKa of a particular compound is what it is written. So for example, between ketone and acetic acid why does the pKa change? Why is acetic acid way more acidic as compared to ketone? So, you can think about all of these different combinations in your pKa chart and figure out or reason why the acidity of a particular molecule is higher or lower, okay.

Thank you.