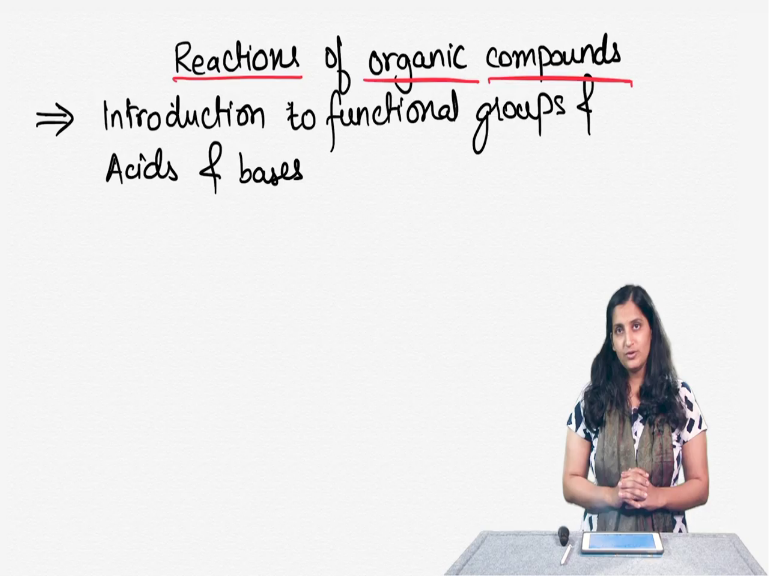
Introductory Organic Chemistry

Dr. Neeraja Dashaputre
Department of Chemistry
Indian Institute of Science Education and Research, Pune

Lecture - 19
Acids and Bases Part – 1

(Refer Slide Time: 00:15)



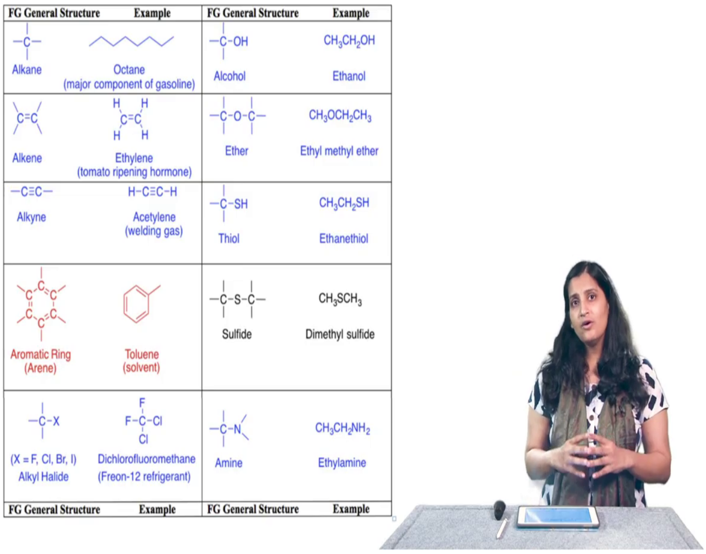
Reactions of organic compounds

⇒ Introduction to functional groups & Acids & bases

Today, we will begin our journey in the vast world of Reactions of Organic Compounds, but before we begin we should look at some of the general rules that govern the reactivity of compounds and we will begin with the understanding of functional groups. So, a functional group is defined as a grouping of atoms in an organic molecule; this grouping or the given functional group exhibits a characteristics set of chemical properties which are largely independent of the rest of the molecule.

As a consequence, an understanding of the chemical behavior of functional groups really allows us to predict the reactivity of the wide variety of organic molecules. So, I do not need to know the behavior of the entire molecule, but if I know the behavior of the individual functional groups that are present in the molecule you can estimate how this particular compound will react in a chemical reaction for that particular functional group.

(Refer Slide Time: 01:17)



FG General Structure	Example	FG General Structure	Example
Alkane	Octane (major component of gasoline)	Alcohol	CH_3CH_2OH Ethanol
Alkene	Ethylene (tomato ripening hormone)	Ether	$CH_3OCH_2CH_3$ Ethyl methyl ether
$-C\equiv C-$ Alkyne	$H-C\equiv C-H$ Acetylene (welding gas)	Thiol	CH_3CH_2SH Ethanethiol
Aromatic Ring (Arene)	Toluene (solvent)	Sulfide	CH_3SCH_3 Dimethyl sulfide
(X = F, Cl, Br, I) Alkyl Halide	Dichlorofluoromethane (Freon-12 refrigerant)	Amine	$CH_3CH_2NH_2$ Ethylamine
FG General Structure	Example	FG General Structure	Example

So, now on screen you are gonna see a table of different functional groups of organic compounds. So, for example, the first one is an alkane. So, you can see that the carbon is connected to all carbons and there is also an example given for each functional groups. So, for alkanes we have already talked about octane and how octane is one of the main components of gasoline that we use for our cars.

The next functional group we want to know is that of the alcohols. So, alcohols are also very commonly used; you must have heard about methanol, ethanol, isopropanol, rubbing alcohol that is used in medicine which is isopropanol; here in the example given is that of ethanol which is the alcohol that people drink. Now, look at the connectivity here. The carbon is connected to an oxygen and the oxygen is connected to a hydrogen. So, if you have this connectivity then you have the alcohol functionality. The next functional group that we want to know is that of the alkenes.

So, alkenes are the compounds with carbon-carbon double bonds. Okay, so, there is a pi bond between the two carbon atoms. Ethylene is the example given and ethylene is more often used for as a tomato ripening agent or tomato, bananas they are, the raw fruit is ripened with the help of ethylene. The next one is that of ether. Now, ether is, that has the functionality of carbon attached to an oxygen and this oxygen is again attached to another carbon right. So, that R-O-R or R meaning any alkyl group right. So, the alkyl group attached to an oxygen and then another alkyl group is typically an ether.

The next functional group you want to know is that of an alkyne and alkyne has a carbon carbon triple bond in it now the triple bond could be in the middle or at the end of the molecule, but it has to have a carbon-carbon triple bond in order to be termed as an alkyne. And, acetylene is one of the very commonly used alkyne which is used in the welding process of metals. Another functional group just like alcohols is a thiol. So, thiol has the functionality of SH instead of alcohol having the functionality of OH and here is one of the thiol examples is given as the ethanethiol; so, CH_3CH_2SH right.

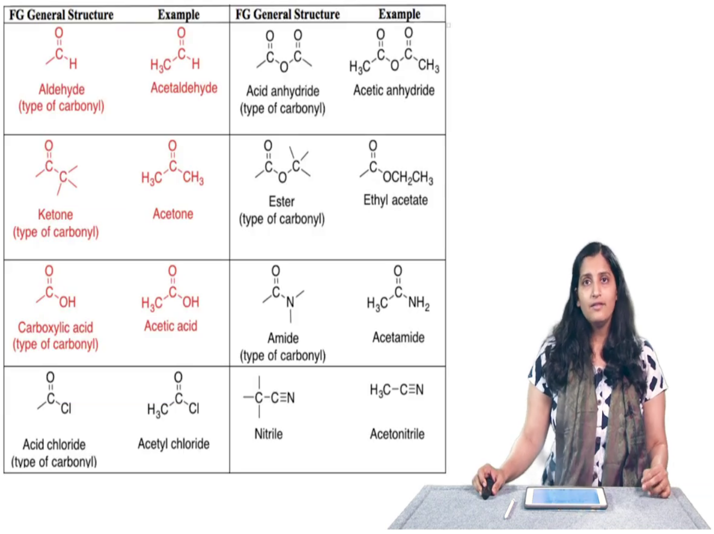
The next one we should know is about aromatic rings. So, benzene ring even though it looks like it is all made up of just double bonds or alternating double bonds, the functionality of the aromatic group or the aromatic ring is very different from that of the carbon-carbon double bonded compound. So, when we look at the reactions, we are going to study the reactions of aromatic compounds differently than from alkenes and we will know why as we go over the reactions.

So, toluene is the example given here, it's a very known common solvent that is used. In fact, most of the drug molecules or the medicines or most of the paints, pigments everything you see around will have an aromatic ring in it and it would be good to go back and look at some of the structures and figure out where all these functional groups are. The next one is that of the sulfide. So, you have a Carbon-S-Carbon. So, just like ether, now this is a sulfur ether you can call it or a sulfide which is carbon, sulfur and carbon bond in it.

One of the main functionalities that we will learn in this course is about a carbon-halogen bond. So, you have either alkyl group attached to a fluorine, chlorine, bromine or iodine which is mainly an alkyl halide in total. So, one of the examples given for alkyl halide here is Freon and Freon is a chlorofluorocarbon and which is really responsible for depleting the ozone layer around earth. So, as you know the refrigerants previously used to use Freon, but now we have stopped using Freon in as a refrigerant in order to avoid the damage that is being caused to the ozone layer.

The next functional group is amine. So, in this case you have a carbon attached to a nitrogen and which can be attached to any R-groups or when I say R-groups I am referring to alkyl groups. So, here for example, ethylamine is one of the examples given for amines.

(Refer Slide Time: 06:19)



FG General Structure	Example	FG General Structure	Example
Aldehyde (type of carbonyl)	Acetaldehyde	Acid anhydride (type of carbonyl)	Acetic anhydride
Ketone (type of carbonyl)	Acetone	Ester (type of carbonyl)	Ethyl acetate
Carboxylic acid (type of carbonyl)	Acetic acid	Amide (type of carbonyl)	Acetamide
Acid chloride (type of carbonyl)	Acetyl chloride	$-C-C\equiv N$ Nitrile	$H_3C-C\equiv N$ Acetonitrile

Now, we are gonna look at some of the functional groups that have carbon-oxygen double bonds. So, you want to look at the whole connectivity. So, when we talk of aldehyde what you have here is a carbon attached to a carbon which is double bonded to an oxygen and the carbon, the double bonded carbon has a hydrogen group. This C=O is very often termed as carbonyl group. So, when a carbonyl has a hydrogen attached to it, it becomes aldehyde.

One of the most known aldehydes is formaldehyde which is used to preserve biological samples or here, in the, in this case the example is given that of acetaldehyde. Again you can look at the connectivity of the C=O to a Hydrogen directly. The another functional group of a carbonyl compound is ketone. Now, in the case of ketones you have two alkyl groups attached to the carbonyl compounds.

So, in this case you have $CH_3C{=}OCH_3$ which is an acetone molecule and acetone is mainly used widely as an industrial solvent, but one of the uses of acetone is also as a nail polish remover. You can also see acid anhydrides; you can also see esters; acid anhydrides have a functionality such that two of the carbonyl groups C=O are attached with the help of an oxygen. Acetic anhydride is given as an example here.

Esters is the next functional group. Now, in esters what we have is a carbonyl group attached to an oxygen, but this oxygen is also attached to another alkyl group or R group. So, it's RC=OOR. So, in this case esters are very commonly used as fragrances in food or candies. The next functional group is that of the carboxylic acid functionalities. So, now, carboxylic acids as you know have to have an acidic functionality. So, it will have a C=O attached to an

OH directly, okay. So, carboxylic acids, one of the main known acid is acetic acid which is present in vinegar which we all use in our food.

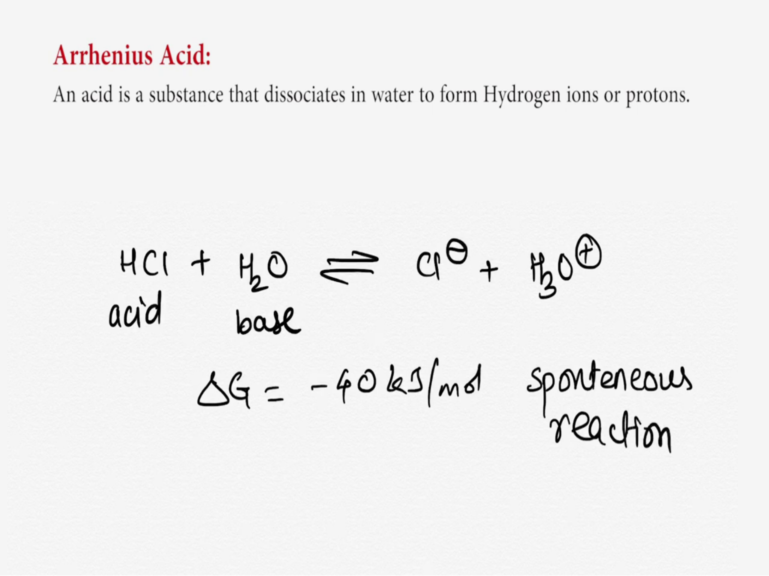
The next one is amide. So, amides have a C=O N, okay. So, C double bond O which is the carbonyl group attached to a nitrogen directly, okay. So, remember in the case of amine, the carbon was attached to a Nitrogen, now in the case of amide you have the carbonyl group, the C=O attached to the Nitrogen. The next one is acid chloride, C=O Cl and the one after that is a nitrile or cyanide; you must have heard about potassium cyanide. So, C≡N is called as a cyanide functionality.

Why I went over all of these functional groups is that right now it would be a good time to recognize the structure of each and every functional group and then trying to be able to remember them because you will see that the functional group really determines what kind of reaction the molecule undergoes in a chemical reaction. So, it would be good to look at different molecules; you can really Google search or you can come up with a lot of chemical compounds around you and figure out what functional groups are present in that molecule.

Typically, you will observe that multiple functional groups are present in a complex molecule which you might be really using in your day to day life. So, it would be good to get acquainted with the knowledge of functional groups. The other tool highly effective in predicting the outcome of organic reactions is actually acid-base chemistry. Many organic reactions either are acid-base reactions in themselves or they involve an acid-base catalysis in the intermediate step.

So, somewhere in the mechanism you will see some kind of acid-base reaction happening. So, it is thus essential to have a good grasp on acids and bases to predict the outcome of organic reactions.

(Refer Slide Time: 10:53)



Arrhenius Acid:

An acid is a substance that dissociates in water to form Hydrogen ions or protons.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons Cl^{\ominus} + H_3O^{\oplus}$$

$\Delta G = -40\ \text{kJ/mol}$ sponteneous reaction

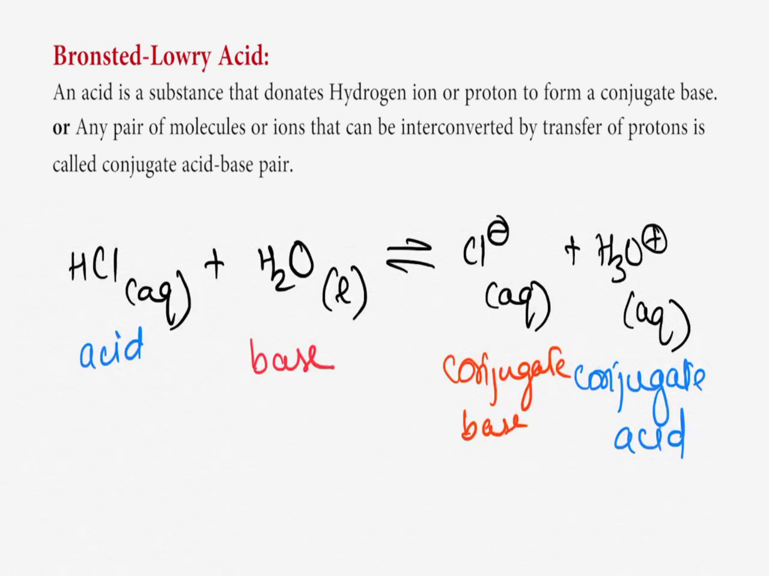
The first definition of acids and bases was really put forward by Arrhenius and I am really revising here what you have learnt in your +2, but let’s just go over it again. So, according to the Arrhenius definition an acid is a substance that dissolves in water to produce H^+. So, I can really write down HCl plus water will give me Cl^- plus H_3O^+ right. So, here in acid which is that of HCl is reacting with water which is a base in order to form H^+ which is really combining with water to form H_3O^+ and Cl^-.

So, according to Arrhenius definition, acid need not react with base; acid only reacted with water in order to dissociate in water. If you really look at the delta G (ΔG) of this reaction, ΔG which really tells us about whether the reaction is gonna be spontaneous or not. The ΔG of this reaction was, is around minus 40 kilo Joules per mole, meaning the reaction is highly-highly spontaneous. Immediately as you add HCl to water it’s gonna quickly form that Cl^- and H_3O^+. So, this is really a spontaneous reaction.

But, if you do the same reaction in gaseous phase, the ΔG really goes close to plus 1300 kilo Joules. Now, when the ΔG is positive we know that the reaction is not spontaneous and in fact, with really high ΔG you can imagine that HCl and water in the gaseous phase do not really interact with each other as vigorously as they do in the liquid phase. So, Arrhenius was really right in predicting that acids have to react with water in order to give off a proton like H^+ in order to exhibit acidity.

The ability of any molecule to behave as an acid really depends on its ability to easily donate the proton or rather dissociate in water. The next definition of acids and bases was given by Bronsted and Lowry.

(Refer Slide Time: 13:25)



Bronsted-Lowry Acid:

An acid is a substance that donates Hydrogen ion or proton to form a conjugate base.

or Any pair of molecules or ions that can be interconverted by transfer of protons is called conjugate acid-base pair.

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons Cl^{\ominus}_{(aq)} + H_3O^{\oplus}_{(aq)}$$

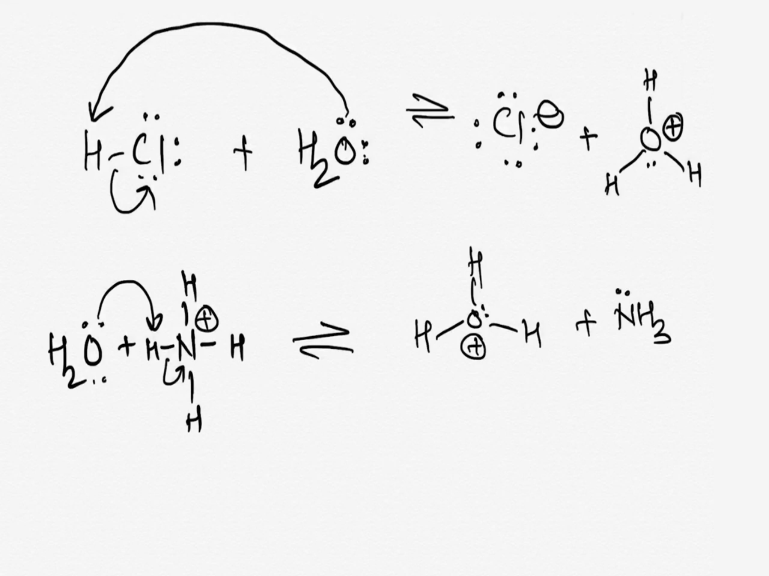
So, Bronsted and Lowry defined that any pair of molecule or ions that can be inter-converted by transfer of proton is really called as an conjugate acid-conjugate base pair, right. So, we are going to look at particular reaction, we will again take the same example. So, herein I am going to take HCl, as I said that it has to be in the aqueous phase, plus H_2O which is in the liquid phase; it's gonna give me Cl^- which is aqueous plus H_3O^+ which is also aqueous phase, okay.

So, Bronsted and Lowry really termed that HCl is going to be my acid here, which is going to react with water which is the base, okay. Now, what it forms as a result is, acid is going to form a pair of conjugate acid and conjugate base. So, now, let us figure out which one among this Cl^- and H_3O^+ is the conjugate acid which one is the conjugate base. So, in order to do that, you just have to think of the reaction going backwards.

Now, as a reaction goes backwards which is the molecule that is gonna function as acid, that is which is the molecule that can give off a proton. So, in this case our conjugate acid is H_3O^+ whereas Cl^- becomes my conjugate base because it has to grab a proton in order to form HCl again. So, that is going to act as a conjugate base.

One of the main things that we follow in organic chemistry is called as a curved arrow notation. So, curved arrows really represent the flow of electrons in a particular reaction. So, now, in order for us to represent this particular reaction let us now draw the curved arrows.

(Refer Slide Time: 15:31)



So, I am going to draw HCl and I am going to draw H_2O; H_2O as we know has a lone pair of electrons or rather two lone pairs of electrons. Now, the curved arrow representation has to start from a pair of electrons or a nucleophile or a negative charge, okay. So, I am gonna go over each one of these examples. So, it has to start from a pair of electrons or a negative charge.

So, I am going to start the arrow from one of the lone pairs on oxygen and I am going to draw the arrow such that it goes and attacks this particular proton. Now, remember if you draw the arrow in the reverse direction it is a wrong arrow. The electrons are not flowing from the proton to the oxygen, even though in the end product it may seem like that the proton and oxygens have formed a bond, the arrow needs to be drawn from the electrons to the positive charge or from the electrons to the proton.

So, you are going to draw the arrow like this. Now, that hydrogen in HCl does not want to form a bond with two things, does not want to form a bond with H_2O as well as the Chlorine; so, what it does is it gives off the electrons of chlorine back to itself. Anyways the bond between Hydrogen and Chlorine is a highly polarized bond such that Chlorine is pulling away a lot of electrons towards itself, right. So, it’s easier for this particular proton to give off that pair of electrons of the bond to the Chlorine.

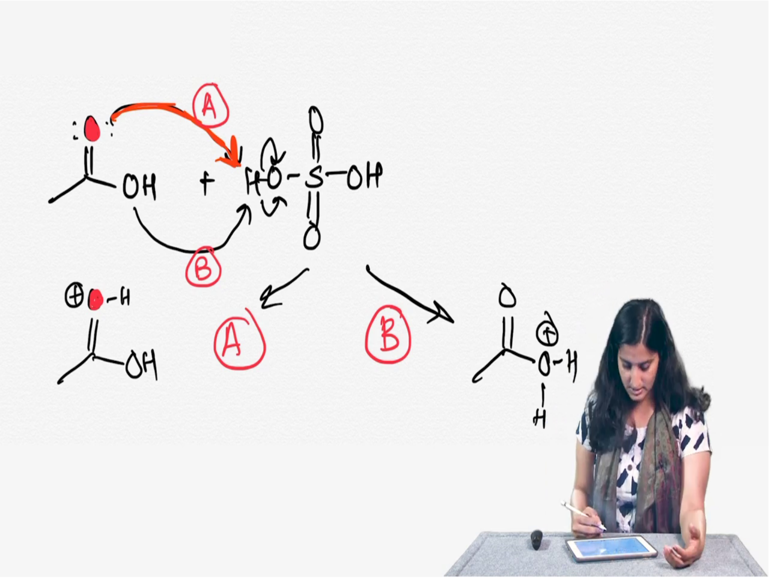
As a result of which the bond between Hydrogen and Chlorine is going to break. So, what’s going to happen is it is going to form a Cl^-, okay. Now, Chlorine as you know had 7 electrons in its lone pair, now with two more electrons it’s gonna have a Chloride a complete octet right and you are going to have a new bond formed between Oxygen and Hydrogen okay, it still has its lone pair.

Now, if you give the formal charge to it you will observe that the formal charge on that oxygen has to be a plus, okay. So, this is how you would represent the chemical reaction in an arrow pushing way. It’s highly important that you master your arrow pushing right now, so that once we go to multi step reactions you can draw arrow pushing for those steps without going wrong. Okay. We will take one more example here.

So, we are going to take water plus NH_4^+. Okay, so, I have an ammonium ion here, okay. So, we are going to draw an arrow pushing reaction between water and ammonium ion, okay. Now, what we start with is, again the arrow starts from the electrons or the lone pairs, and, or the negative charge and goes off to the positive charge or the proton. So, in this case the electrons are present with oxygen.

So, it’s gonna grab a proton. As it attacks that proton, the proton does not want to form bonds with two entities. So, what it does it gives off the electrons back to NH_4^+ and in the result what happens is you give rise to H_3O^+ and NH_3, okay. So, these are some of the examples; practice your arrow pushing.

(Refer Slide Time: 19:43)



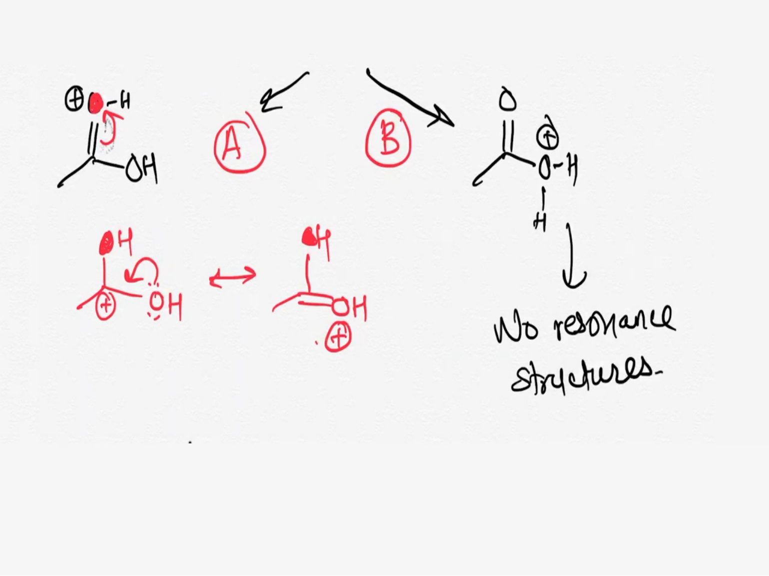
Now, we are gonna just have a quick look at different types of Bronsted – Lowry bases where in there are two or more receptor sites. So, in this case water had only one receptor site that is the Oxygen, but what happens when you have more than one receptor sites. So, we are going to look at a reaction between acetic acid and H_2SO_4.

So, we are going to look at acetic acid which looks like this and H_2SO_4 which looks like this, okay. When we look at this particular reaction you can see that both the molecules are really, can function as acids and both the molecules can really functions as bases as well, but one of the key things to remember that H_2SO_4 which is a strong inorganic acid or mineral acid is probably not going to behave as a base. So, what we are going to do is we are going to make the acetic acid act as a base and attack on this H_2SO_4.

Now, the question arises which one of the two oxygens should we start with? So, let me now just color one of these oxygens, okay. So, one of them is red Oxygen, the other one is the black and white Oxygen. Which one of it will go and attack the proton? That's the question. So, what I am going to do is let us attack with this proton and you will form this particular structure or if we attack it with the other proton; let me just draw a colored arrow for reference; if we attack it with this other proton you will form this.

So, now the question is which one of these two scenarios A or B really exists, right. Okay, so, what we need to then look at is, what is the product and we have to look at whether the product is stable or not? In order to define the stability of the product we are going to look at the resonance structures.

(Refer Slide Time: 21:59)

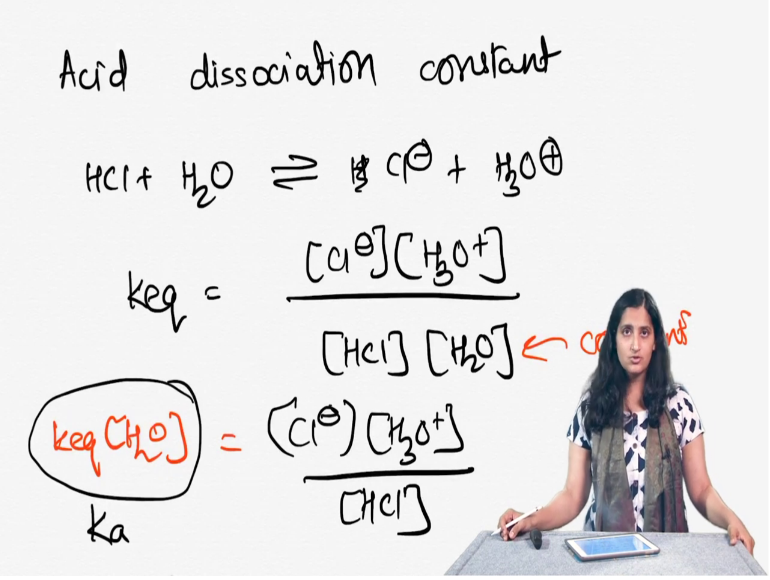


So, in this case if I draw the resonance structure for this one I can draw looking like this, right, where in this goes up, right. It also has one more resonance structure when this oxygen puts electrons here, right. So, the molecule A really has two resonance structures that it can work with right whereas, if you see B there are no resonance structures possible for this molecule.

Again, going back to resonance structures you can remember that in order to draw the resonance structures we are only allowed to move pi electrons or non-bonding electrons right. So, we cannot really break sigma bonds in order to draw resonance structures. So, as you can see A gives rise to a couple of resonance structures and that's why it is more stable. So, it would be right to attack with that oxygen.

So, when I have to predict the basicity of acetic acid I would say that the more basic oxygen in the case of acetic acid is the carbonyl oxygen. It is the oxygen that is attached to the carbonyl group, okay.

(Refer Slide Time: 23:25)



So, now, let us have a look at acid dissociation constant. And you must have heard about these as well or learned about these, but now we are going to look at them from the point of view of organic compound. So, the strength of any acid is represented by an equilibrium constant. So, I am going to take the same reaction,

$$HCl + H_2O \leftrightharpoons Cl^- + H_3O^+$$

So, that's our reaction.

Now, the K equilibrium which is the equilibrium constant for this particular reaction is given by concentration of products over reactants. So,

$$Keq = [Cl^-]\ [H_3O^+]\ /\ [HCl]\ [H_2O]$$

Now, if you really think about it, the way we have carried out this reaction is that we have taken a part of water and we have added a small amount of HCl into it. So, if you really see that throughout the reaction the concentration of water that is the big jar of water it has not really changed, right.

So, we can say or we can term this particular concentration of water as a constant, okay and we can take it to the other side. So, I will have,

$$Keq\ [H_2O] = [Cl^-]\ [H_3O^+]\ /\ [HCl]$$

This term here Keq into concentration of water is also called as Ka, okay.

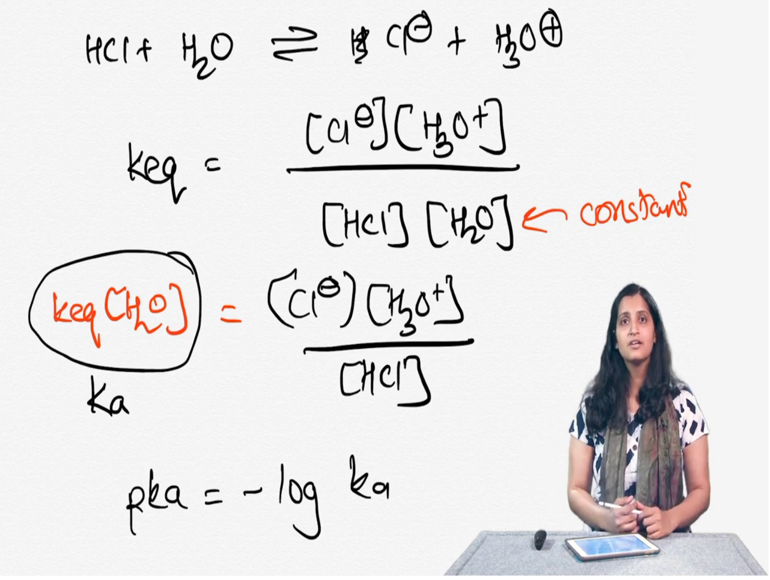
$$Ka = Keq\ [H_2O] = [Cl^-]\ [H_3O^+]\ /\ [HCl]$$

So, which is the acid dissociation constant and this acid dissociation constant has been determined for multiple acids including organic and mineral acids and which mainly predicts if the acid is going to behave as a strong acid or a weak acid.

So, knowing the Ka’s is actually kind of important. But, if you really look at the values of these Ka’s it’s very difficult to remember them. So, for example, the Ka of acetic acid is around 1.8 X 10^{-5}, right. So, it’s really-really low because acetic acid is very very weak acid, it does not dissociate in water. So, if I have 100 molecules of acetic acid in water, hardly one of them will dissociate to form acetate and H^+ whereas, in the case of HCl almost all the HCl molecules are going to dissociate. So, that tells me the difference between weak acid and strong acids.

Most of the organic acids are very very weak acids. In fact, acetic acid is one of the stronger organic acid. So, you can imagine all the other organic molecules are going to be really-really weak meaning that acid dissociation constants are also going to be very very low and which are going to be very difficult to remember.

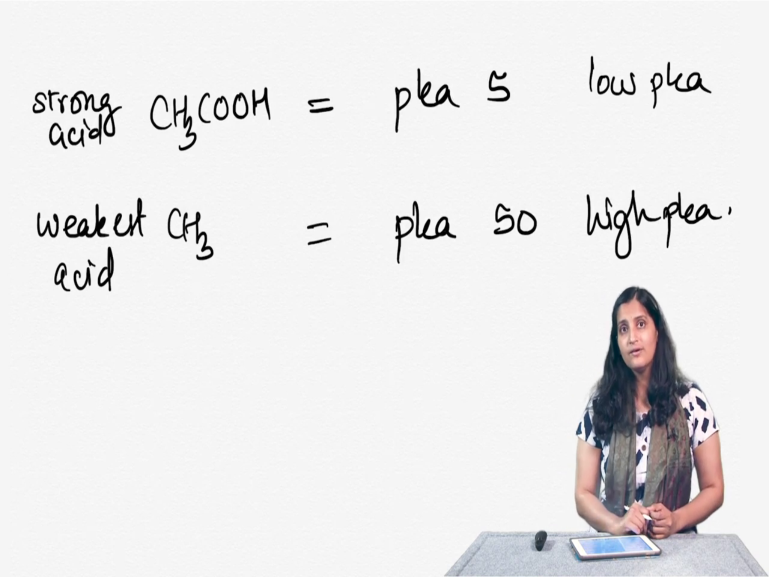
(Refer Slide Time: 26:49)



Hence chemists have come up with a scale which is the pKa, or a new term called as the pKa which is, pKa = - log Ka

This is just for convenience. This, there is absolutely no reason why we cannot work with Ka if needed we can also work with Ka, but in order to avoid remembering a very very small number it might be better to really remember the negative log of it such that it becomes easier to remember.

(Refer Slide Time: 27:21)



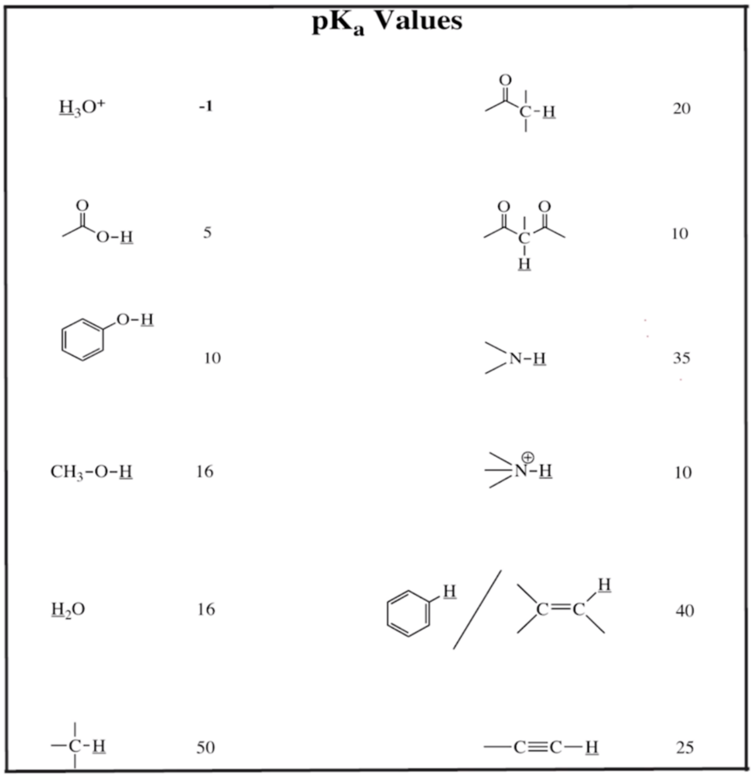
strong acid CH_3COOH = pka 5 low pka

weakest acid CH_3 = pka 50 high pka.

So, now what we are going to look at is we are going to look at acetic acid. So, acetic acid as I said is one of the stronger organic acid. So, acetic acid has a pKa close to 5 okay; on the other hand, let us take a very weak acid. So, let us take methane. So, I am going to write your strong acid and weak acid for convenience. Methane is probably one of the weakest acid, okay. So, methane does not like to give off a proton and becomes CH_3^+ right. So, methane has a pKa close to 50 or more than 50, okay. As you can see the strong acids have a low pKa whereas the weak acid have a correspondingly high pKa, okay.

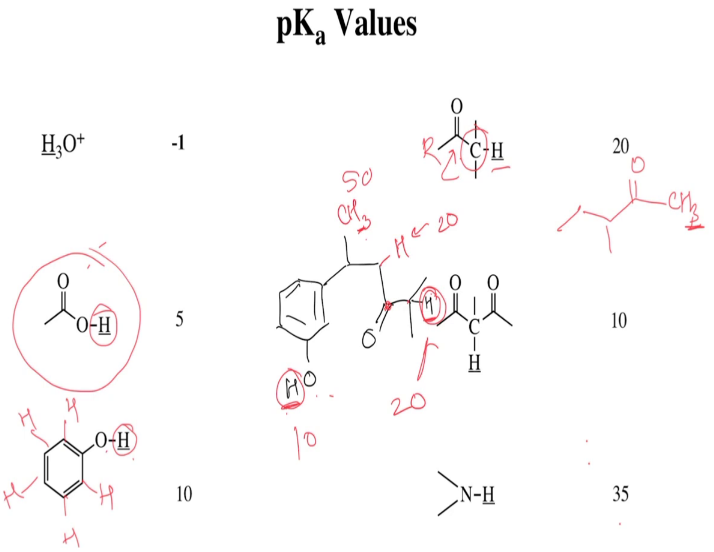
So, it would be good to know that given a pKa you can predict if the acid is strong or weak. So, one of the good things to remember is that strong acids have low pKa’s and weak acids have high pKa’s.

(Refer Slide Time: 28:37)



So, now, what I want to look at is a table. In this table you can look at the different pKa's of different functional groups and I will also go over how to refer to this pKa chart because this pKa chart is very very helpful in predicting the outcomes of organic chemistry reactions.

(Refer Slide Time: 28:51)



So, now, let us look at this particular first molecule here, it is the pKa of H_3O^+ that is close to minus 1. One thing I want to clarify is that the pKa's in this chart are not exact.

For example, the pKa of acetic acid here, it's not exactly 5 it is close to 4.76, but 4.76 is way tedious to really remember and what you will understand henceforth is that you need not know the exact pKa of an acid and the conjugate acid to predict the outcome. We want to know a ballpark number, something that will give us some indication about roughly what is the pKa of the acid or the conjugate acid. So, all the numbers in this chart are not exact, they are close to what they are.

The second thing I want to talk about is about the kind of molecules that we have in this table. So, if you see then you will see different types of protons; protons meaning the hydrogen atom that is getting abstracted in the acid-base reaction, right. So, in the first one we have H_3O^+ which will have a pKa of around minus 1 and the second one is acetic acid which will have a pKa of around 5.

Now, acetic acid, look at the proton that is underlined. This particular proton gets subtracted in the acid-base reaction. So, when you refer to the table please look at each and every proton that is underlined. We are talking about that particular proton not any other proton in the particular molecule. So, for example, here in I have a phenol molecule and we are talking about the O-H pKa, the proton in that O-H we are talking about the pKa of that. Remember, there are other hydrogens, but that is not the hydrogen. So, for example, the aromatic carbons all of them have hydrogens on them we are not referring to that particular proton, we are referring to the O-H proton.

The next thing I want to point out is this particular table is very helpful in predicting the pKa of very similar molecules. So, for example, if you are tomorrow asked a pKa of propionic acid which is one more carbon than the acetic acid. The pKa of propionic acid is going to be roughly around 5, okay; you can of course, predict the pKa whether it will be higher or lower than the acetic acid pKa, but you need not know exactly the pKa of propionic acid.

You can always refer to it as acetic acid has a pKa of 5, propionic acid will also have very similar pKa close to 5 right. So, that becomes helpful because now what I have is a chart that tells me pKa in the ballpark range for most of the organic molecules right. So, for example, let's say that we have a hydrogen attached to a carbon and that particular carbon is attached to the C=O and then a R-group; R meaning any alkyl group right.

So, this is a ketone. Most ketones will have a pKa close to 20. Of course, I can modify it right and still the pKa will be close to 20, it could go to 21, it could go to 19, but it will be in the right ballpark around 20. So, when you are referring to this chart make sure that you know how to read the chart; first thing is the underlined proton, second thing is the which proton are we really talking about.

So, let's say if I give you a complex molecule right and if I ask you a question what is the pKa of this particular proton? It will be 10 because it is a hydrogen attached to an oxygen and that oxygen is attached to a benzene ring. You see a very similar situation here which is hydrogen attached to an oxygen which is attached to the benzene ring.

So, what I have is this particular proton here, it's going to have a pKa close to 10, it could be higher or lower, but write in the ballpark range. If I ask you what is the pKa of this particular proton here. Now, that proton is a hydrogen attached to a carbon, right, hydrogen attached to a carbon and the carbon is again attached to another carbon which is of C=O. So, this pKa will be close to 20, right. You can also refer to this one, this one will also be around 20 which is on the other side of the C=O.

Now, if I take this alkyl group pKa that particular proton is going to have a pKa close to 50 because it is a hydrogen attached to a carbon; the carbon is again attached to a carbon or hydrogens right. So, that kind of situation is seen in this case the pKa is close to 50. So, based on the kinds of attachments you have you can figure out the pKa of any proton using this particular chart. One good thing to know is the use of pKa in figuring out which proton will get abstracted first.

So, right now in this molecule the proton that will get first abstracted by a base is the one that has the lowest pKa. So, right now the phenolic OH that hydrogen on that phenolic group will be the first proton that will get reacted in an acid-base reaction. The next one would be the one that is next to that carbonyl group because it has a little higher pKa right so, it will be abstracted next or the third one that very very difficult to picked out will be the alkyl group, right.

So, I would strongly suggest not to waste time in remembering each and every detailed pKa, but rather remember this chart because it gives you an approximate value. So, for example, acetic acid does not have the exact pKa of 5, it is 4.8 something (4.81), but we don't need to remember that. We just need to remember that carboxylic acids like acetic acid will have a pKa close to 5 and that is enough for us to go forward and predict the reactivity of the most of the molecules.

So, the reason chemists care about pKa a lot is because it gives us a quick guide line about how a reaction mechanism is gonna happen. Acid and base reactions are one of the quickest steps that happened in the chemistry. So, they are one of the fastest steps so, they will happen first given any two molecules reacting. If there is an acid-base reaction possible that's the first reaction that will happen. So, that's why chemists love to work with pKa's and predict the mechanism of the compounds.

So, in the next class we are going to go over why different functional groups have this particular pKa's.