hello everyone in the last two lectures we talked about the physical and chemical properties of alcohols and then we moved on to understand the different ways in which the alcohols can be synthesized especially starting from alkenes and carbonyl compounds as substrates then the next we moved on to making diols with the help of dihydroxylation reaction starting with olefins and taking permanganate kmno4 and osmium tetroxide as the dihydroxylating reagents

so with that synthesis and the chemical and physical understanding of alcohols let us in today's class understand the reactivity pattern the reactions which are you know different types of reactions which the alcohols undergo

so today's lecture will essentially be dealing with the reactions and reactivity of alcohols that is what we are going to learn today the reactions of alcohols but before we start we should understand what is the kind of reactivity the alcohols have by virtue of the hydroxyl functional group

so we have a hydroxyl functional group which is sitting next to the alkyl part and just look at the structure you have an you have a hydroxy group sitting next to your alkyl and this imparts some kind of important electronic property to this molecule

so this hydroxyl group in which oxygen is more electronegative it pulls the electron density is more electronegative than hydrogen as well as from carbon

so because of this electronic effect this bears a delta negative charge and both hydrogen and carbon bear a delta positive charge

so if we understand this reactivity of this molecule now we can say that broadly the reactions of alcohols can be classified into two parts one which involves reactions due to hydroxyl group and the other which in which the entire molecule is covered okay

so both the alkyl and the hydroxyl group that means the entire part of the molecule is covered in giving you the reaction

so in the hydroxyl group also we can further sub classify it as the reaction in which only the hydrogen atom is replaced

so reactions involving replacement of hydrogen atom ok and the second could be the reactions in which the hydroxyl group is replaced

so you are replacing the o h group

so these are the broad classifications of how these reactions can happen

so if you are replacing the hydrogen atom that means you are cleaving this o h bond and as we discussed in the previous lectures the relative acidity of the alcohols follows the order 1 degree 2 degree and 3 degree which tells us that the 1 degree alcohols are the ones in which the hydrogen atom replacement is going to be the fastest if you replace the hydroxyl group these are the reactions which you can well understand will be substitution and elimination reactions of alcohol

so substitution and elimination is what is going to involve a replacement of the hydroxyl group ok

so if we

so so that is pretty obvious that if you have a methanol if i am comparing the acidity or you have a tertiary butanol right

so in this case if i have to compare the acidity of this bond and this bond you can well understand it by the effect of the three methyl groups versus one methyl group

so it is going to change the bond strength of the o h bond and the stability of the complementary conjugate base which is going to get generated from each of the two alcohols next when we compare the acidity constants of alcohols with other molecules

so let us see and compare the acidity constants of alcohols with other molecules ok so let us take the simplest of all water and see how they behave with respect to water in terms of their acidity

so the pka value of water is known to be 15.
74 if i take the simplest alcohol methanol the pk value of this molecule is 15.
5 i take ethanol pk value of this is 15.
9 you take a tertiary butanol the pka of this molecule is 18.
0 and then you move on to the other classes of compounds like the acetylene and alkyne you take it in reference with hydrogen which is 35 you take the nitrogen containing molecule ammonia which is 38 and then you can compare it with a regular alkane and ethane which is 50.

so now if you look at the pk value of these molecules they are increasing which tells you that the relative acidity is decreasing which means that the alkane

so if based on that i have to plot the order of acidity in general for these molecules i can say water is the most acidic followed by the general class of compounds alcohols followed by alkynes followed by hydrogen then amines and then alkane

so this is the relative order of acidity of these different classes of compounds but since we are talking about alcohols in particular would like to say that in alcohols with the exception of methanol all the other alcohols are weaker acids than water

so all alcohols except methyl alcohol or methanol are weaker acids than water

so when we talk about this acidity behavior we have to understand it in terms of the stability of the conjugate base

so what is happening in this reaction that you have an alcohol okay and when you are saying that it is acidic what is happening in this equilibrium reaction

so this alcohol is giving you after losing a proton it is giving you an iron which is a alkoxide ion okay you are generating an alkoxide ion and this is your protonated form of water this is what is happening essentially when we are saying when we are talking about the acidity constant of alcohol

so in this the acidity depends upon two factors generally it will depend upon the strength of this o h bond which will again depend upon the nature of the alkyl group and it also depends upon the stability of the conjugate base

so we are talking about the conjugate base okay the general norm is that if you have a strong acid we will have a weak base that is how it goes but not only should we have a weak base we should have a stable base

so there are two factors when you talk about these alkoxides ok and i compare an alkoxide of a sodium methoxide ok versus or potassium tertiary but oxide suppose i take this i compare these two bases and i look at the stability of these two bases okay now this being a small base this can easily undergo solvation right it can undergo solvation but this being surrounded by three methyl groups the center this is a bulky base and it undergoes because of crowding less solvation and that is what you are seeing in the trend that methanol was a stronger acid right because it has a weak base in terms of the order of the basicity of these bases i can say that the order of basicity will be that sodium methoxide is a weaker base as compared to hydroxide and then you move on to ethoxide the same order which we saw for the corresponding acids or the alcohols of these bases

so the order of basicity for these corresponding conjugates bases arising from these species is going to follow this order which tells me that this is the strongest base and this is the weakest way

so we were comparing or tertiary but oxide with a methoxide and this is a stronger base okay and therefore the corresponding tertiary butanol is a weaker acid so so these things are based upon two factors as i pointed out one it depends upon the electronic effect of the r group okay and second it depends upon the extent of solvation of the conjugate base which again will be dependent upon the r group the steric factor which allows it to undergo extensive hydrogen bonding with the solvent molecules and get stabilized or not

so with this understanding on the acidity behavior of the alcohols we now move on to see what are the reactions it is offering as a result of this hydrogen replacement ok

so we come to the first class of reactions which is the reactions replacing hydrogen atom

so the reactions replacing hydrogen atom as we just saw i can conveniently write follows the order one degree two degree and then three degree alcohols this is the order of reactivity of the alcohols in terms of the ease with which they are able to replace the hydrogen atom

so the first reaction in this series would be the reaction with active metals which we did earlier also in the previous class when we were talking about the acidity behavior of these alcohols we did it previously with active metals such as sodium potassium aluminium

so these are the reactions in which the alcohol is reacting with the base and it is giving the corresponding alkoxide with the evolution of the hydrogen gas

so this could be a sodium metal or in general if i have to write it could be any of these active metals you can even have magnesium in these series

so you can in general saying that the met this reacts with the metal and it gives you the corresponding alkoxide and this gas

so this is the basis on which we previously also discussed about the formation of the potassium tertiary but oxides and the aluminium tertiary but oxides which are used as bases in organic synthesis ok the next reaction which ah talks about the acidity of these alcohols is the reaction with grignard's reagent grignard's reagents we know are able to abstract any acidic proton very easily okay

so grignard's reagent essentially react with active hydrogen species

so they react with active hydrogen species and the substrate in this case happens to be alcohol

so the when the alcohol reacts with grignard reagent it forms it picks up this hydrogen okay

so this hydrogen is picked up by the alkyl part of the grignard region and what you get is the corresponding alkane and romgx

so which tells you that this is the stronger acid as compared to this which is a weaker acid ok the third type of reaction could be when you have the alcohol and you treat it with organic acid when we say organic acid it is any carboxylic acid okay with organic acids in presence of an acid catalyst ok

so it could be any acid catalyst we take h2so4 and if you could remember and recollect we talked this reaction earlier also when we were talking about the method of preparing the alcohols from esters and there we said that dsterrification is the pathway

so you took an alcohol you took an acid you reacted the two in the presence of an acid and you formed an ester the reverse reaction is what is going to furnish you the alcohol back from which the ester was synthesized

so we are talking right now about the forward reaction in which the alcohol and the acid react to give you ester okay

so you take the acid this is a acid catalyzed reaction

so the first step is the protonation ok and this i can conveniently draw its resonating structure in which you see that there is a carbocationic species which is present okay

so the next step it is again a reversible step and you have attack of the alcohol onto this carbonyl of the acid and this gives you this is followed by loss of a proton from here ok and you get this species and then there is elimination of water molecule and you are left with this carbon bearing a positive charge and then this can be reorganized to show in this manner which eventually undergoes loss of proton to give you the corresponding ester

so this is the reaction in which the esters are obtained when you treat an alcohol within acid

so these this is your building block and this is an acid catalyzed reaction which is giving you an ester and if you look at this reaction this this involves the replacement of the hydrogen atom of the alcohol

so that is why we are saying that this is another reaction in which this is replaced and this or goes and attaches itself to the carbonyl of the acid another reaction similar type which furnishes the esters but with another activated substrate of an acid is with acid chloride or anhydride

so this reaction is essentially the same which we just discussed with the acid but in this case instead of the acid we can take acid chloride or we can take the corresponding anhydride and both the cases the product which we get is an ester ok

so the reaction is quite straight forward you take you take the acid chloride treated with the alcohol and the product is an ester ok mechanism is essentially the same ok you start with this you have an activated carbonyl here

so directly it is attacked by the alcohol o h group and you get this kind of an intermediate which then undergoes the loss of chloride because this is what has to quit in order to give you the reaction

so you get again this intermediate which then undergoes a loss of proton ok to give you the corresponding ester

so this is another reaction in which we are getting esters not from acids in this case but from acid chloride and s or or any of its anhydrides ok the next reaction in this series would be with the corresponding phosphoric acid

so so far we have talked about the carboxylic acid we can also have phosphoric acid giving you similar kind of esters which in this case will be phosphates

so we see that when we have the alcohol treated with phosphoric acid just the way we treat it with carboxylic acid we got the corresponding carboxylate ester in this case when you treat it with phosphoric acid what do you get

so the alcohol is treated with h3po4 this is the structure of phosphoric acid as you can imagine in case of carboxylic acid there was one o h group right attached next to the carbonyl in this case you have three hydroxyls which are attached next to the p double bond o

so we expect or we do not know if each of these are going to get replaced

so the first thing which happens is elimination of a water molecule and you get the corresponding product in which one of the o h is is replaced by o r and this is called alkyl dihydrogen phosphate ok

so you have alkyl dihydrogen phosphate this is what you get but the reaction does not stop here it can react with another molecule of alcohol with the elimination of water it can give you the next product which is going to be the second hydroxyl substituted by o h by o r and what you get is this product which is dialkyl hydrogen phosphate ok

so this is what you get now and since there is one more o h available it can react with one more molecule of alcohol to give you eventually the all phosphorylated product which is a tri alkyl phosphate

so what you get in this case is a tri alkyl phosphate and we know that these phosphates esters of phosphoric acids are important in biochemical reactions

so when you look at this phosphate what comes to our mind is atp right which is adenosine triphosphate so these esters of phosphoric acids these are important when we talk about the biochemical reactions

so this is another instance where you can see that your o h is cleaved and o r is what is attaching to the phosphorus unit to give you mono dye and tri alkyl phosphates ok going ahead in this series the next reaction is very interesting and it has a very important use also this is a reaction in which the hydroxyl group is converted into a good leaving group ok

so your hydroxyl is converted into a good leaving group what do i mean by that

so what is happening in this reaction is that the alcohol is treated with

so this is a reaction with alkane or adenine sulfonyl chloride ok

so just now you were treating with the phosphorus based reagent and now you are treating with the sulfur based reagent which is a alkane or arene sulfonyl chloride given by the general formula we can say can be r so2cl or ar so2cl

so the interesting thing here is that this alkane sulfonyl chloride this could be a methane sulfonyl chloride ok

so this could be a methane sulfonyl chloride and when you treat an alcohol with a methane sulfonyl chloride you get the corresponding sulfonates which we call as mesylates

so these mesylates are nothing but these are methane sulfonate esters ok you get methane sulfonate esters

so what is a general reaction we will talk about that but before that if you treat it with if your ar happens to be paratoline sulfonyl chloride okay we say paratolvine sulfonyl chloride you treat it with this the corresponding compounds which we get are called tosylates okay in this class methane sulfonyl you can also treat it with trifluoromethane sulfonyl okay

so you can treat it with trifluoro methane sulfonyl chloride and in this case the compound which you get is a trifluoromethane sulfonate ester which we call as the triflates

so all these are you know important compounds because they are good leaving groups and they are widely used in synthetic organic chemistry when a hydroxyl is transformed into these tosylates mesylates right triflates and then it is used for subsequent functionalization

so the reaction i am going to write here involves the reaction of your alcohol general reaction you treat it with any alkane or aryne sulfonyl chloride in the presence of pyridine as a base and what you get is the corresponding sulfonate ester with the elimination of hcl

so now you can well rationalize the reason for adding pyridine that it is used to take away this hcl which is generated during the reaction and form this pyridine hcl salt ok

so it is basically to neutralize the hcl

so the mechanism which goes into this reaction is the following you take the alcohol treat it with the sulfonyl chloride

so the reactivity of this sulfonyl bonds you can well visualize will be you know both ways you can have this is the kind of reactive it is going to have but let us show with one of these oxygens

so this is going to be attacked by the alcohol right

so in the presence of pyridine your reaction is happening

so what you get is this intermediate ok

so you get this intermediate which is unstable and immediately undergoes loss of chloride iron to give you now this proton which is already acidic is picked up by the base okay and what you get is your corresponding sulfonate ok

so this is a sulfonate which you get when you treat an alcohol with the sulfonyl chloride you are getting the sulfonate esters which are good leaving group and because they are good leaving group they are widely used in the substitution reactions in which you have a nucleophile and you have converted an alcohol into its sulfonate and this eases the substitution reaction to give you the corresponding substituted product with the release of the sulfonate because it is a weak base ok the sulfonates and it is a very good leaving group that is why the alcohols are generally converted into these sulfonates for substitution reactions the next set of reactions is the reactions replacing o h group

so far what we did was the reactions in which the hydrogen atom was replaced now we are going to talk about the reactions in which the entire o h is replaced and this i told you essentially we have the substitutions and the elimination reactions

so again there can be very many ways in which the o h group can be replaced the most important one is with halogen acids

so we talk about halogen assets

so what do you mean by halogen acid it is represented by the general formula h x where x is your halogen your x could be iodide bromide or chloride ok

so your halogen acids can be either a dry hx gas which means you can have either dry hi hbr hcl or you can also use concentrated aqueous forms of these acids okay

so we can have concentrated aqueous acid either of these forms the reactivity of the halogen acid follows this order that the iodo is the most reactive followed by the bromo followed by the chloro and that is what imparts you know difference in the conditions under which each of these substitutions with the assets can be carried out for example if we use h i we generally keep the temperature below 100 degree centigrade

so it is a much milder substitution if you keep hbr you can use either concentrated hpr or you can also have in situ generation of hbr by using a salt like a potassium bromide or sodium bromide and treat it with concentrated sulphuric acid

so when we reflux it these are the conditions when we use hbr as the reagent if we use hcl hcl is a weaker chloride is a weaker nucleophile okay and it will not react the way the iodize and bromide does okay because it is a weaker nucleophile

so for using hcl we use concentrated hcl along with anhydrous zinc chloride which we know behaves like a levis acid you must have come across these in the friedel crafts reaction

so we add zinc chloride which act as a levis acid and we carried this out this reaction out under heating

so these are the different conditions in which each of these halogen acids has to be used depending upon the difference in the reactivity pattern of these acids okay

so the reaction is a substitution reaction you would have guessed by this time it is a substitution reaction okay and since we are using an acid this reaction is also an acid catalyzed reaction ok reaction with halogen acids is a acid catalyzed reaction

so what is the need of an acid you are working with an alcohol you treat it with hx you are getting the corresponding halide with the elimination of a water molecule but we say it is an acid catalyzed reaction the reason for using an acid here is that the acid protonates the alcohol okay it protonates the o h of the alcohol and makes it a good leaving group

so this is probably the same thing we talked a few minutes ago that to convert it into a good leaving group you are converting into the corresponding sulfonates because o h itself is not a good leaving group

so it is a acid catalyzed reaction which protonates it and makes o h a good leaving group and facilitates the substitution okay so what is happening with the different kinds of hydrogen halides

so if you have the alcohol okay and you treat it with let us say the hbr ok it is a simple substitution reaction you get the corresponding bromide and this is about it if you use the corresponding chloride we are saying that this is not working for this one and the ease with which a bromine is able to replace a hydroxyl is not the same with which a chloride can do

so and there is no reaction if you just use the concentrated hcl for carrying out the substitution

so in this case an additive is added which is your zinc chloride i just said behaves as a levis acid and what does it do is it activates your hydroxyl by coordinating here and you form this kind of an intermediate which is then quite active

so your oxygen is bearing a positive charge ok and then your halide which is a chloride in this case which comes from hcl ok this is now able when it attacks this it is able to form the corresponding alkyl halide easily because of this bond polarity induced with the help of the zinc chloride ah salt and then you get zn oh cl2 this is formed along with or you can also represent it like oh zn cl2 which then undergoes in the presence of the acid it forms zncl2 with the elimination of water

so this is added as a levis acid and this reaction you would have also come across it is a test for confirming what is the type of alcohol if you are able to guess this your zinc chloride and hcl it is also known as the lucas reagent ok you might have come across this reagent name and this is a reagent which is used for distinguishing between the primary secondary and tertiary alcohols

so what it does is when you add this lucas reagent to a one degree alcohol it gives no turbidity this is the visual interpretation that there is no turbidity okay if you add it to a two degree alcohol we say the turbidity appears in five minutes and if you add it to three degree alcohol we say the turbidity appears immediately

so the question is what is this turbidity due to this is what the reaction is we have shown you that the chloride is replacing hydroxyl you are forming alkyl halide and this reaction is carried out under aqueous condition

so when you have this alkyl halide formation this is what it imparts turbidity to the reaction to your solution because of its insolubility in the aqueous media

so when you have a three degree alkyl light immediately it gives you turbidity because of the formation of the 3 degree alkyl chloride okay let us see a few examples with which these halogen acids are able to substitute i will take a few examples you take n pentyl alcohol

so you start with n pentyl alcohol which is a one degree alcohol you treat it with hcl and you have to add anhydrous zinc chloride and heat it because otherwise the reaction will not go and then under these strong conditions what you get is the corresponding n pentyl chloride this is how these alcohols react with the halogen acids to give you the corresponding alkyl halides if you start with the two degree alcohol let us say you start with isopropyl alcohol you treat it with concentrated hbr or the other bromide source could be nabr with h2so4 under reflux conditions as we just discussed you get the corresponding bromide okay if you take a 3 degree alcohol tertiary butanol for this you need much milder conditions ok you treat it with concentrated hcl even at room temperature this gives you a tertiary butyl chloride and this we saw is based upon the reactivity of 3 degree alcohols is much more as compared to 2 degree as compared to 1 degree this is what we just saw

so the second method now will come across a second method which is used for this kind of substitution and this is when we treat the alcohols with phosphorus halides just now we saw that alcohols react with phosphoric acid to give phosphates now we are going to talk about another phosphorus based reagent which are phosphorus halides which could either be pcl3 a pcl5 pvr 3 which is phosphorous with bromine it could be phosphorus in iodine all these reactions when we treat the alcohol with this we get the corresponding alkyl halides

so these are the phosphorus reagents which are used for conversion of an alcohol substitution with the halide

so you treat alcohol with lets say pcl5 the products which you get is an alkyl halide alkyl chloride in this case and pocl3 along with elimination of hcl

so this is a general reaction which goes but what is the mechanism how are these formed and what is the you know kind of pathway this reaction is adopting

so you have roh and you have pcl5 okay

so if you have five chlorines attached to phosphorus pcl5 the first step is loss of one of the chlorides here ok and what you get as a result is this intermediate you get this intermediate and this is followed by loss of h plus and c l minus that means is a loss of hcl here and what you get is this intermediate okay which eventually

so in the presence of the chloride ion okay the chloride ion comes and picks it up here and what you get is this product which is your alcohol substituted with the chlorine okay

so in this reaction alcohol can also react with phosphorus in bromine pbr3 is the reagent it gives you alkyl bromide along with formation of po3 okay and if you balance this

so will be three molecules of alcohol giving you three molecules of alkyl halide and the mechanism for this reaction can be rationalized like this you have alcohol reacting with pbr3 the trigonal structure

so the first instance is the removal of the br minus to form this intermediate ok

so this is kind of a sn2 type of displacement in this case that the br minus leaves this comes and then this is a protonated essentially this is a protonated alkyl dibromo phosphite okay this is a protonated alkyl dibromophosphite and this then in the presence of br minus essentially the same thing is happening as was in the previous case this goes and attacks here

so what you get is rbr plus this and which can again since there are two bromines present here it can again react with two molecules of alcohol right and undergo loss of these two brs to give you two molecules of alkyl bromide along with formation of this acid which we can say is a phosphorus acid ok i will give you few examples how these alcohols react with pbr3 and what are the other implications involved

so when you treat it with pbr3 this is a primary alcohol okay this is two methyl one butanol

so obviously it is a one degree alcohol we expect it to undergo sn2 type of reaction and what you get is the corresponding two methyl one bromobutane if you start with a two degree alcohol which is one phenyl ethanol under the same conditions bromination with pbr3 you will end up getting the complementary brominated product which is one bromo one phenyl ethane and since these are going by sn2 pathway okay

so one degree or two degree alcohols easily undergo this bromination and in this there is no carbocation formation obviously if it is going by sn2 pathway there is no carbocation information there is no rearrangement unlike as was witnessed in the case with halogen acids that there was the carbocation forming was undergoing a rearrangement since there is no carbocation there is no rearrangement specially when you carry out this reaction at or under 0 degree centigrade and therefore we say that pbr3 is the preferred reagent for alkyl bromide formation ok

so for these reasons this is the reagent of choice when we have to carry out or make the bromides or from the alcohols all right

so this was about the alkylation with al with halogen acids and with phosphorus reagents let us look at another reagent for carrying out the halogenation of alcohols which we call as a thionyl chloride ok

so with thionyl chlorides and the reaction with alcohols is very interesting again because in this case it is a very clean reaction ok you start with the alcohol treat it with thionyl chloride in the presence of pyridine you get the corresponding alkyl halide with the evolution of sulphur dioxide and hcl both of which are gases ok

so we say it is a very clean reaction and especially suitable for formation of alkyl chlorides which otherwise if you use a halogen acids require much harsher reaction conditions okay

so you can have a primary alcohol you treat it with socl2 in pyridine you get the corresponding halogenated compound ok

so it is an important reaction for synthesizing the chloroalkanes and the mechanism which goes into this reaction can be interpreted like this you have a sulfonyl chloride socl2

so based upon the reactivity pattern obviously we expect that this bond is polarized and this is what is going to be the first line of attack and what we get from here is this intermediate okay which instantaneously undergoes loss of this cl minus to give you the corresponding intermediate and now since we have pyridine in the reaction medium it picks up this acidic proton and we get the alkyl chloro sulphite ok along with formation of this pyridinium salt and then eventually the last step is that your alkyl chlorosulfite which is formed ok in the presence of pyridine undergoes this reaction when you get the alkyl halide along with formation of intermediate which eventually results in loss of sulphur dioxide along with the regeneration of pyridine

so this is the overall mechanism of the reaction in which you can see that sulphur is eliminated as the so2 gas

so this is a good method for the synthesis of the alkyl chlorides ok

so now we move on to the third type of reaction in which we have reactions involving both the alkyl and the o h groups okay

so so far what we have studied is if it is only the o h bond breaking hydrogen is getting substituted or the entire o h functionality is getting substituted now will lead the reactions the third type in which both the alkyl and the o h groups are involved and in this we have three types of reactions one is an oxidation reaction which involves both parts another type of reaction is a dehydrogenation reaction and the third part on this is a dehydration reaction

so these are the three types of reactions in which both the alkyl as well as the o h groups are involved and will take up each of them one by one let us talk about first of all the oxidation reaction oxidation of alcohols

so oxidation of alcohols is looks to be a very trivial reaction but it is a very interesting reaction because there are a number of oxidizing agents which are available today for carrying out the oxidation of alcohols to different species ok

so a number of different oxidizing agents are available

so we can have alcohols again depending upon the fact they are primary secondary or tertiary they have different ease with which they can get oxidized they can different products which can be obtained as a result of their oxidation and the kind of oxidizing agent which is used to carry out this kind of transformation what we are going to discuss today are the reagents based on manganese 7 and chromium six species ok so number of oxidizing i mean if i go on and you know telling you about the type of oxidizing agents available it can be a one full course in itself but we will restrict ourselves to manganese 7 and chromium 6 the traditional and the most well studied oxidizing agents for oxidation of alcohols for manganese 7 the reagent which we use is kmno4 potassium permanganate it can be used under acidic conditions

so we have acidified kmno4 or it can be used under alkaline conditions in which we have alkaline kmno 4 both these reagents are able to carry out the oxidation of one degree alcohols directly till the acid okay

so if you take a one degree alcohol let us say you take this alcohol and you treat it with kmno4 it is going to oxidize it all the way till the end till you get the corresponding acid if you treat it this alcohol with kmno4 the corresponding acid which you will get is this

so you can see that if you started with one two three four five carbon system you end it up with one two three four five carbon system in the acid that means there is no loss of carbon atoms when you are carrying out the oxidation of an alcohol till the acid and another important feature of the kmno for oxidation is the change in the color which is also used as a test to see if the oxidizable functionality is present in the molecule

so you start you treat it with basic aqueous kmno4 solution ok which means you have kmno4 basic means you have under alkyl line you put some hydroxide it is aqueous and you heat it you get the corresponding potassium salt of the acid first which then gives you the corresponding acid along with the formation of a brown precipitate of mno2

so you started with the basic aqueous kmno4 solution which was purple in color and you ended up with a brown ppt that means this reaction is taking place and there is an oxidizable functionality which is changing the color of manganese from purple to brown the other important reagent in this series as i said is a chromium 6 reagent and a chromium 6 reagent again can be used in different ways the most popular and important ones are we used chromium trioxide in dilute h2so4 and this mixture is taken in aqueous acetone okay this reagent when you take and dilute h2so4 chromium dioxide it generates what we call as the chromic acid

so it gives you chromic acid which is h2 cro4 and this reagent is known as the jones reagent it is the popular jones reagent which is used for the oxidation of alcohols ok you can

so one you can use the chromium trioxide or you can directly use the chromic acid or sodium chromate in h2so4 water mixture which again can carry out the oxidation of any alcohol or one degree or two degree into the corresponding aldehyde or ketone

so what is

so interesting about this jones reagent or the put the chromium based reagents is that if you start with the alcohol and you treat it with the chromium reagent which is orange red in color you get first of all the corresponding aldehyde if it is a one degree alcohol you stop at the aldehyde stage along with the formation of chromium three plus ions which are green in color but the reaction is difficult to stop at this point and it further in the presence of the available chromate ions gets converted into the corresponding acid but what is visually appealing here is that the orange red color of your solution changes into light green because of the presence of these chromium ions

so when you have a kmno4 solution your purple color changes to brown but if you have a dichromate your orange color changes to green and these are the visual indications that an alcohol functionality is present in the molecule

so let us now look at the mechanism of this oxidation with chromic acid and more importantly that if you have a one degree alcohol right it first reaches up to the aldehyde stage and then it goes finally up to the acid when you treat it with the chromium based reagent for carrying out the oxidation

so let us see the mechanism how it works

so you start with the alcohol i am taking a one degree alcohol you treat it with chromic acid okay the first step is the loss of this water molecule to give you a very important but unstable intermediate

so chromium here is in the oxidation state six right and here also it is in the oxidation state six you get this intermediate which is a chromate ester you get this chromate ester which is unstable it cannot be isolated ok

so the next step is immediately that since you are working under aqueous conditions the water molecule you get the corresponding oxidized alcohol this is the oxidized form of the alcohol along with formation of this reduced chromium species ok

so you have a reduced chromium species which can be written as h c r o three minus and the oxidation state of chromium here is four

so we have oxidation of alcohol to aldehyde and we have chromium six getting reduced to chromium four species which eventually through complex disproportionation and oxidation reactions it forms a chromium three species a mechanism of which i am not going to discuss here today but you have to understand that this green color is because of the formation of the chromium three species which is getting generated from hcro3 minus which is getting generated during the reaction it gets again it can get protonated here hcro3 minus you are working under acid conditions to give you this molecule which is h two c r o three

so now the point is that the reaction does not stop here and let me also talk about the change in the oxidation states which is happening

so you started with the alcohol in which the formal charge on carbon was minus one okay when you oxidized it till the aldehyde stage the formal charge on carbon now becomes plus one

so this tells you that this is an oxidation reaction of alcohol to aldehyde the minus one is changing to plus one

so you are gaining two here

so you are losing two here

so this is an oxidation and your chromium 6 is changing to chromium 4 and it is a reduction process with the gain of 2 electrons we move on now to see that what happens that this reaction does not stop at the aldehyde stage and it further continues on all the way to give you the acid

so you have now the aldehyde with you okay under aqueous conditions what is happening this is delta plus delta negative you get this intermediate and you can also write this rewrite this as this intermediate which is an unstable aldehyde dihydrate okay

so it is an aldehyde dihydrate which is formed when the aldehyde is there under acidic aqueous conditions

so once the aldehyde forms a dihydrate next series of steps is the same as were for the oxidation of the primary alcohol as we just saw that there is loss of a water molecule there is formation of this chromate ester ok the same sequence of reactions and then eventually this is lost as the presence of water this is lost as an acid along with formation of this chromium species which can further take up the proton to give you h2 cr o3 you