

welcome to iit pal program today we will discuss oxidation of aldehydes and ketones

so aldehydes has been found to differ with ketones in oxidation

so first we will discuss oxidation of aldehydes and either strong oxidizing agents like  $\text{KMnO}_4$  acid also mild oxidizing agent that will discuss little bit later

so in aldehydes there the carbon atom is retained but will now seen ketones it slightly differs

so if  $\text{C}-\text{C}$  bond breakage then this will this two acid will form and it is important that ketones in ketone oxidation the bond breaking happens also possibilities is another possibility is this one and here  $\text{C}-\text{C}$  bond black pinch some examples if you oxidize acetophenone then you get benzoic acid plus now we will discuss how you differentiate aldehydes and ketones and two test can be done where aldehydes will respond and ketones will not respond first is that tolerance test another is heating test

so first we will discuss tolerance test

so what is tolerance reagent now it is ammoniacal silver nitrate

so this reaction is done under basic medium

so if aldehydes are treated with ammoniacal silver nitrate and then this silver mirror can be seen and aldehydes will respond

so what is failing test failing test plus you will get some what are three molecules

so as you know this cupric solution then cupric sulphate is blue and cupric oxide you will get red brown and another important thing that only aliphatic aldehydes

so tolerance test generally both aldehydes both aromatic and aliphatic aldehydes will respond but here only aliphatic and tolerance its failings reagent is basically two solution which is called failing a it is

so c it is mixture of helling a and b and generally before the reaction you have to mix filling and b in equi molar quantities and then you have to treat with aldehydes

so it is alkaline jelly

so what is the if you mix them what will it form c

so by dented complex of pattern is form and which is blue in color now we will discuss one special reaction which is halo form reaction and this name comes from because in this reaction halo form like iodopharm will generate

so what is the reaction

so aldehydes and ketones having

so so the oxidizing agent is sodium hypo halide and the product is

so carboxylic acid having one less carbon atom and that carbon atom goes to the halo form and halo form

so methyl group attached to carbonyl we can think that this group should be present

so only aldehyde that can give test is the acetaldehyde because if you put any other except hydrogen and it becomes ketone also it has been observed that this kind of compound the alcohols which are oxidized which are oxidized in situ to the ketone can also respond to the halifan test

so what is the test now will this see c which is generated by sodium hydroxide plus halogen

so you get sodium hyphaelite and then you get and if it is x is equal to iodine then you get  $\text{CHI}_3$  and this is iodophorum this is called iodophone and you get yellow precipitate and this is then test also that compound ketones and aldehydes having a  $\text{COCH}_3$  group when you treat with sodium hyphallite or sodium hypo iodide you get this you will precipitate

so we can discuss example suppose if you treat with acetophenol and discuss also the mechanism

so if you treat acetophenone with base what will happen this will discuss little later now also that  $\alpha$  C-H acidity

so this  $\alpha$  carbon ion is formed and which can be resonance stabilized by enolate and then suppose if it is iodine then it reacts with iodine and then you get this one and then repetition

so all three hydrogen is replaced by iodine and then the base is present so then it will hydrolyzed

so base if attacks you get this one and since this is quite stabilized now with three iodine

so you get this one benzoic acid and minus C minus I<sub>3</sub> and which because this strong acid it will be put on it will put on it the iodo form and you get the precipitation of iodophor in the reaction

so this is base mediated reaction

so we will discuss some more examples which concern the acidity of the  $\alpha$  hydrogen

so acidity of  $\alpha$  hydrogen will discuss little bit now

so carbonyl compounds which have  $\alpha$  hydrogen it can be like this also that high color

so this hydrogen is acidic and it is due to two reason one is the electron withdrawing carbonyl group is there

so which is present also  $\alpha$  position of the  $\alpha$  C-H also if you deprotonate it by base just in the  $\alpha$  reaction we have seen that you get resonance stabilization

so resonance stabilize stabilization of the carbanion and this is important because when the delocalization of charge happens then it gets more stabilized now we will discuss some reactions which concerns the acidity of  $\alpha$  hydrogen and first one is aldol condensation aldol reaction

so aldehydes and ketones which have  $\alpha$  hydrogen

so if they are treated with dilute alkali this with base a little bit dilute alkali then then beta hydroxy carbonyl compound beta hydroxy aldehyde that is called aldol or beta hydroxy ketone this is called ketone is formed and this is called aldol reaction

so we will discuss example little bit

so suppose if you treat acetaldehyde dilute H<sup>-</sup> then what will happen

so this is beta hydroxy aldehyde and this is actually aldol product and if you heat it then the dehydration will happen and you get  $\alpha$  which is unsaturated and that reaction then it will be called aldol condensation

so if you only get this one then its called aldol addition but if you heat it and elimination of water happens and you get  $\alpha$  unsaturated aldehyde then its called aldol condensation reaction similarly ketone also like acetone this is mild base barium hydroxide you get and this keto is also sometimes is the general term the aldol is used also

so this is addition product and if you heat then you get the  $\alpha$  unsaturated and

so the aldol common term is used for both aldehydes and ketones ketol is not so much huge

so aldol condensation and here you see only same molecule is used to equivalent and that is called homoaldol also and we will discuss little bit now cross aldol reaction cross aldol reaction means between two different aldehydes two different ketones okay and when both aldehydes suppose both aldehydes have  $\alpha$  hydrogen then there is possibility of four products like if you treat acetaldehyde and propanaldehyde

so you see both as alpha hydrogen and that means there will be the four possibilities the homoaldol condensation and then cross aldol condensation and then in the cross aldol one will be donor acceptor another case another will be donor acceptor

so we will see what will be the aldol dehydration products

so this is when this is called homo aldol condensation this is homo aldol condensation and another two products will be formed from cross aldol

so what is that

so you can get this product

so when acetaldehyde will be accepted and propanaldehyde is do not another case and in this case acetaldehyde is the donor and this is acceptor

so these are cross aldol products

so as you can see as you can guess that if the number of alpha hydrogens of compounds where the  $\alpha$  carbon is there then there is a mixture of products but if one of them does not have alpha carbon then you can get selectively one product like reaction between acetophenone and benzaldehyde

so acetophenone has alpha carbon this alpha carbon is there but in benzaldehyde there is no alpha carbon no alpha hydrogen actually there is no alpha carbon to this side

so there is no alpha hydrogen

so what happens if you treat with base this is a donor and this is acceptor

so if you heat it

so this parts come from acetophenone and this is a benzaldehyde

so if you treat it base and then heat it

so it is aldol condensation product a similar reaction can be thought with a star if you treat with this and then heat you get one three ketone one three diketone

so the enolate reacts and ethanol is eliminated

so you get this one and this called claisen condensation

so aldol condensation is the reaction of carbonyl compounds where alpha hydrogen is present now there is another reaction where aldehydes respond and it does not have alpha hydrogens and that is called canis reaction

so who will respond aldehydes no alpha hydrogen and you need strong base

so compared to aldol reaction here mild base or mild waste is sufficient but here in this case you need strong base and in this reaction what happens gets oxidized too another molecule gets reduced to alcohol

so this kind of reaction is called disproportionation reaction

so this is this disproportionation

so we will discuss examples like formaldehyde formaldehyde does not have any alpha carbon

so there is no question of alpha hydrogen like concentrated  $\text{KOH}$  and you have to heat it then you get

so you get potassium formate it is the acid actually and then you get methanol similarly benzaldehyde benzaldehyde also is we saw that in a aldol reaction it accept as donor and it does not have any alpha hydrogen

so two molecules of benzaldehyde reacts and if you heat it

so one molecule gets oxidized to the benzoic acid and here it is salt now and another molecule gets reduced to benzyl alcohol we will discuss cross aldol condensation reaction and cross aldol condensation reaction is generally different aldol condensation with without alpha hydrogen

so it has been found if formaldehyde

so this is important when  $\text{LiAlH}_4$  does not have alpha hydrogen they are non oxidizable

then what happened for formic acid is formed and alcohol of this aldehyde gets generated

so the selectively the formaldehyde gets oxidized but the other non eligible aldehyde gets reduced

so why is that that we will see now and also we discuss the mechanism of candida also

so what happens the formaldehyde does not have any other group or group that's why that is why the electrophilicity of formaldehyde is more compared to other aldehydes

so if you treat formaldehyde with hydroxide in presence of other aldehydes the hydroxide and selectivity goes to the formalden because it is more electrophilic more electrophilic and then suppose if you treated benzaldehyde this is the important step here since this is acidic

so it will be it will deprotonate its proton and you get the benzyl alcohol after acid treatment i am sorry that that i forgot to remove the oxidation term in some slides because some reactions are not oxidation reactions now we will discuss an aldehydes application and uses

so formaldehyde is disinfectant and it generally kills almost all bacteria that's why it is used as biological preservative former benzaldehyde also has nice almond flavor and that's why it is used as flavor compound in many foods like ice cream candy etc similarly cinnamon dehydrate also cinnamon flavor citral also uses antiseptic also as perfumes and vanillin that's why drawn structure in the first class is also important compound and it has vanilla flavor and we conclude here thank you