

myself punya murthy from deepander chemistry iit
guwahati i welcome you all to iit paul program in this class we will study
about
the reactions of carboxylic acids and for our ah convenient we will divide
the reactions into four types the reactions that involve cleavage of o h bond
so first we will see the reaction where
the cleavage of o h bond basically acidity of carboxylic acid then we will
see
the reaction of copper silica acid where the cleavage of c o h bond takes
place
for example the formation of anhydride and ester formation following that we
will see the
reaction of the transformation of carboxylic acid into the corresponding
derivatives for example
reduction of carboxylic acid to alcohols at the end we will see and the
functional group will be
intact but part of the molecule and where the ch bond will be converted into
a
functional group for example the reaction in the case of benzoic acid where
the aromatic c-h bond can be converted into nitrobenzene and
so on for example in the case of benzoic acid
and the c-h bond can be converted into a nitro group and then we will end up
with
a nitrobenzyl acid cleavage of o h bond carboxylic acid acidic in nature they
can give
proton and make salt with bases for example when you take the carboxylic acid
react with base for example sodium hydroxide it can form sodium carboxylate
and water as by product
so this is a base this acid that acid can due to
the acidic nature of carboxylic acid it can keep the proton can form salt
sodium carboxylate
and where you generate water by product and it can also react with big base
like sodium bicarbonate to give the corresponding carboxylate water and carbon
dioxide this is a test we
use in the laboratory to find out and whether the compound that we have is
capacity gas or
not and if you treat with sodium bicarbonate and you can see the formation you
can see the
evolution of carbon dioxide then you can tell that the compound has capacity
acid functional
group this is one of the tests we use in the laboratory to find out the
carboxylic
acid functional group in organic compounds and this is when you react with the
base and
you can make salt carboxylic acid also can react with the electro positive
elements
uh metals like sodium can for example it can react with sodium can
form again sodium carboxylate hydrogen gas
so now let us see the acidity of carboxylic acids carboxylic acids are big
acids and
when you take an aqueous medium they can undergo dissociation to carboxylate ion
plus hydronium ion
so partially they can undergo dissociation
they exist in equilibrium both you can find the the undissociated carboxylic

acid in water as well as the dissociated carboxylate ion and hydronium ion they exist in equilibrium this depends upon the strength of the acid is not like mineral acid like hcl which can undergo complete ionization in to Cl^- and H^+ but in this case since it's weak acid partially it can undergo dissociation to give the carboxylate anion and hydronium ion this depends upon the strength of the acid the acid is stronger acid it can undergo dissociation more and you can form the corresponding carboxylate ion if it is weak acid partially it can't form the concentration of this will be less comparing to the undissociated carboxylic acid

so this can be described the extent of dissociation of the carboxylic acid in aqueous medium can be described using this equation this is the acid dissociation constant

so the concentration of dissociated carboxylate

and the concentration of carboxylate ion and hydronium ion in water in moles per liter

divided by the concentration of the undissociated carboxylic acid this called acid dissociation

constant and if the acid is stronger then we have higher integer value and for our convenient

we always express the strength of the acid as pK_a equal to $\log K_a$ the strength of the

acid can be explained using this pK_a value and this is a integer value and if the pK_a is less

the acid is stronger and pK_a is more that acid is weaker this you can see this is always if

you see the textbook the right pK_a of this acid and carboxylic acid and the stronger acid always

will have less pK_a comparing to the weaker acids and why carboxylic acid is acidic

why this this can be explained by the resonance of carboxylate ion if you take the formic acid for example the bond length is different this is shorter this is the longer the bond length when you make the corresponding carboxylate ion this resonance structure of the carboxylate

ion this can be drawn like this we see the bond length of this one is one point two seven ohm strong

so now the bond length is same in both case

so this because of the resonance this

carboxylate ion stabilizes that leads to that makes the carboxylic acid acidic in nature

and the stabilization of the carboxylate anion can be explained by the delocalized by

molecular orbital of the carboxylate anion as this is sp^2 hybrid carbon and now you have unutilized p orbital and this unutilized p orbital of this oxygen and overlaps with this p orbital of this carbon and p orbital of this oxygen and make delocalized

localized by molecular orbital as you can see here like this this the

delocalized by molecular orbital and if you look at it you have two electron lone pair this sp^2 orbital has a lone pair and you have one electron one electron and you have the three atoms four electrons they are delocalized and above and below the plane and make this carboxylate anion is more stable this is the responsible for making the carboxylic acid acidic in nature and this is because of this stability of the carboxylate anion via resonance now let us look at the effect of substituent in the carbon atom for example if you have electron withdrawing group a carbon atom so the if this carboxylate anion has electron withdrawing group the acidity of carboxylic acid increases because it takes electron from the carbon atom it makes more acidic it can easily give the proton on the other hand if you have electron donating group on the carbon atom it can reduce the acidity of the carboxylate so for example let us take formic acid this unsubstituted carboxylic acid when you introduce a methyl group so to the carbon atom this is a methyl group as you know this is electron donating group it can give electron to the carbon atom so this compare this is more acidic compared to this because if you look at the K_a acidity constant of this this will be this will be more acidic comparing to that when you introduce electron with the donating group the acidity of the carboxylic acid is decreased and when you go for K_a further this will be again less acidic and because the ethyl group can give more electron towards to the carboxylate carboxylic functional group make less acidic in nature and this acidity order of when you have the alkyl group and when you have the in the case of aliphatic carboxylic acids and when you have the electron donating group and so like this and the acidity this unsubstituted the formic acid is more this is called methanoic acid right its IUPAC name is more acidic comparing to the ethanoic acid and ethanoic acid is more acidic comparing to the propionic acid and this is on the other hand now let us look at the acidity of this compare the acidity of ethanoic acid this carboxylic acid so one of the sp^2 C-H bond can be replaced by a C-Cl bond and one of the hydrogen has been replaced by Cl so chlorine is as you know is an electron withdrawing group now the acidity of this is increased this more acidity compared to this because when you have the electron withdrawing group when you have the electron withdrawing group the acidity increases and for example if you replace two hydrogen atoms you get the $Cl_2CHCOOH$ this is more acidic and if you introduce

another hydrogen replace with a chlorine you get this most acidic among these ah four

compounds the acidity is this more acidic see again this is the most statistic so when you

have introduced the electron with the drawing group therefore the acidity of the copper slick

acid increases and similarly when you introduce a electron donating group the acidity of carboxylic

acid decreases this acidity of carboxylic acid when you introduce different substituents they

affect the acidity of carboxylic functional group now let us look at the cleavage of the reactions

that involve the cleavage of c o h bond when you have cover when you heat carboxylic acid for example ethanic acid with acid like or like p2o5 it can

readily undergo dehydration to give anhydride these two molecule of ethanoic acid combine

together to form the unheighted and you water has been can be has been removed by the phosphorous bond oxide

so the removal of water from this reaction by heating using phosphorusburn dioxide can

produce the anhydride this water this the oh group the c a carbon o h group has been cleaved this you make here co and bond and you make

unhydrated this is one of the uh very important reaction because we use uh unhided

as precursor for oscillation reactions and when you have the carboxylic acid with the

past treat with the possible spent oxide you can make anhydride basically it removes

this water molecule phosphorus pentoxide remove the water molecule and you make anhydride

and also you can make treat with acid it can also when you heat the copper like acid with acid it

can undergo dehydration to give unhydrated this there are so many methods available

this one of the method that we use to make anhydrides from capacity acid the second reaction is esterification and if you have a carboxylic acid for

example ethanoic acid you

can react with alcohol for example methanol the presence of acid or base say reversible reaction for example if you treat

with the acid they can undergo reaction to give methyl state this ester you take opposite acid and alcohol they can

react the pressure acid under heating to give ester this called methyl estate and you produce water and this can exist in equilibrium reaction therefore

whenever we do the esterification we have to take one of the this is called fischer esterification

you take one of the reactant excess and as a solvent and then you can push the reaction forward

to get a sufficient yield or if you want to make a good yield then you have to remove this

water from the reaction mixture by isotropic distillation and

so on here also for example you

should not have the water the water is removed by using the phosphorus pentoxide if you have

water then it will go back the reaction you have to remove if you remove the water then you can get good yield of the ester this is also a very useful reaction to make ester because and acid can be readily converted to ester then we can do several organic transformations now let us see the mechanism of this reaction protonation of the carboxylic acid can form this intermediate once you have the protonated carboxylic acid this can undergo addition reaction with one to addition reaction with alcohol can form this tetrahedral intermediate so proton transfer from this intermediate from this intermediate once you form this this proton transfer if you remember the the first part of the carboxylic acid we studied the mechanism of how you can ester can be cleaved into carboxylic acid and alcohol the same mechanism here and this you have the water the water can ah remove this proton and you make the hydronium ion that hydronium ion again you can react with this oh you can give this uh intermediate it's basically proton transfer takes place first remove this proton and by using water as base you make the hydronium ion that hydronium ion again can react and you can make this intermediate this intermediate can transform into the ester this can be further converted into a protonated ester can be ah transformed to the ester so this is the mechanism how the acid reacts with the alcohol the pressure acid to give ester and this an equilibrium reaction the third example is the transformation of acid to acid chloride for example this propionic acid when you react with a phosphorus pentachloride or thionyl chloride it can be converted into so the acid chloride that o h bond that carbon o h bond undergoes converted into carbon c l bond see this also very important precursors we use as precursor for oscillation reactions the acid can be converted to the corresponding acid chloride once you form the acid chloride it is more reactive more electrophilic in nature now compared to the carboxylic acid now we can add a nucleophile and we can and easily the reaction can be carried out and the advantage of this reaction there are so many methods available and so one of the efficient method to make acid chloride is to reaction with thionyl chloride and where you generate sulphur dioxide and hcl as gas they can go and you will end up with a few product that will be easier to get pure acid chloride the third example is the reaction of carboxylic acid with ammonia to produce amides for example take benzoic acid when you react benzoic acid with ammonia when you pass it can first it can form the salt any carboxylic acid when you react with ammonia it forms from the salt once you form the salt and when you heat the

salt it can convert into amide it's also very useful reaction and if you have copper slick acid and ammonia and you can make the salt when you heat the salt it can give the amide

the case of benzamide you will get but if you use the aliphatic capacity acid you will get the corresponding amide and you can also use in case of if you use um the dicapripusalic acid for example

so when you react with two equivalent of ammonia then you make the corresponding ammonium salt this when you heat you get amide so this can be further converted into imide this is called imide is called thalidom thalimalde

and you can see first you can form the salt when you heat the salt you get the amide that can be further converted into imide and where you by removing one molecule of ammonia

so far we have seen four example

on the cleavage of c o h bond in carboxylic acid and first we have seen the formation of anhydride when you treat with the press of dehydrating agent like phosphorus

pentoxide and acid can be converted into anhydride and then we have seen um the esterification

reaction of capacity acid with alcohol the piece of acid or base they can be converted into the

corresponding ester the third example we have seen acid can be readily converted into the

corresponding chloride acid chloride uh using a reagent like phosphorus pentoxide

chloride PCl_3 or thionyl chloride or oxalate chloride these are the common reagents used to convert carboxylic acid to the corresponding acid chloride then the acid chloride is the carbonyl carbon of acid fluoride is more electrophilic

nature they can readily undergo now additional reaction with the nucleophiles at moderate

conditions to get selectively the addition product then we have seen an example for how you can convert

carboxylic acid into the corresponding amide and first when you add ammonia then

they form salt that salt when you heat it converts into the corresponding amide by removal of water molecule the next reaction is the reaction of c o h group

so we are going to look at two reactions two

type of reactions first one is a reduction of capacity acid for example if the propanoic acid it can be readily

converted into the corresponding alcohol this called reduction reaction

and the carboxylic acid is reduced to the alcohol this case and the common reagent we use for reduction of lithium aluminum hydride or diborane based reagents they can readily

reduce the carboxylic acid to the alcohol and of course you have to during the reaction you have to form the salt which can do the workup when you react

with water then you can get the alcohol

so this very one of the important reaction how do

you convert the alcohol to acid to alcohol but you cannot use other reducing agent like

sodium borohydride they don't reduce of course sodium borohydride you have to use like iodine

recently found that can reduce but lithium aluminium hydride is commonly reduced to reduce carboxylic acid into alcohol this reaction usually carried out in the of he reflects and you make the aluminum alkoxide that aluminum alkoxide when you do the work of and you can get alcohol it is a very useful reaction and we often use functionalized or any carboxylic acid can be selectively reduced for example in the case of amino alcohol you can reduce the carboxylic acid to the amino alcohols the next example is decomposition reaction when you have the carboxylic acid when you treat this carboxylic acid with base and you can convert to the corresponding carboxylate or simple capacity gases also when you react with soda lime so it undergoes decarboxylation in this case you will get if you use ethanoic acid you get methane and if you use benzoic acid under this condition it will be converted into benzene and sodium carbonate so any carboxylic acid when you have and you treat with soda lime a heat they can undergo decarboxylation to give the corresponding this is called decarboxylation reaction the fourth type of reactions is reaction that involves C-H bond for example when you take this in this reactions the carboxylic acid functional group is intact and this part of the C-H bond part of the molecule undergoes reaction and we will see two examples one is Hell-Volhard-Zelinsky reaction where for example if you have carboxylic acid that contains alpha hydrogen atom so this carboxylic acid when you react with chlorine or bromine the pressure of red phosphorus it can be halogenated and red phosphorus followed by hydrolysis and the X can be Cl or Br it can be selectively at the alpha carbon can be halogenated the corresponding carboxylic acid for example if we are then you can get alpha-bromo propionic acid this very very useful compound this compound and can be further converted into a variety of molecules basically is a building block for example this compound for example let us consider this as two-bromo propionic acid this we can further react with for example sodium cyanide you can do cyanation this of course you can do hydrolysis you can get the dicarboxylic acid and similarly when you react with energy to minus you can make amino acid alpha-amino acid if you react with OH⁻ you get lactic acid derivatives so lactic acid you can form so this is very very useful reaction and this alpha-halo carboxylic acid can be converted into different molecular compounds by an equilibrium substitution reaction this is a substitution this is a nucleophile and easily can react this is a very reactive one and you can convert it into cyanoacetic acid or hydroxycarboxylic acid amino copper amino acid alpha-amino acid lactic acid and cyanocapric acid and

so on the other example is functionalization of carboxylic acid and for example aromatic capacity acid for example when you react this benzoic acid with the nitro group you can form nitro benzoic acid you can get nitro benzoic acid and similarly when you react with the cyano group you can get sine of benzylic acid always this in this case the electrophile undergoes reaction at the meta position carbon number this carbon atom not here this can be explained by the you write the reaction pathway y selectively or the n mode to the electrophile undergoes substitution at the metacarbon atom not the para orthocarbon atom and this can be explained because this copper silica acid is electron with the drying group and because of this always the electrophile undergoes reaction at a substitution reaction the metacarbon atom not para one on other hand if you have electron donating group and of course this the reaction will take place with para position this can be explained by writing the resonance structure of this reaction this electron with the drawing group when you add the electrophile suppose the electrophile takes place at the meta position you will have this sigma complex will have it so if you write a resonance form of this ah sigma complex can the another structure is so this can transform into product if you look at this restaurant structures this benzene ring attacked this nitro electrophile and first you form this intermediate sigma complex this complex can be written different resonance forms if you read the regional structure of these intermediates and always look at it this carbocation is present at ortho position you can see here and are paraposition so the electron when you have the electron with the drawing group and if it undergoes electrophilic if if you add the if you see and this carbocation present ortho position already this is the electron withdrawing group and this is the if you see add the nitro group and so this is the these two carbons have less electron density otherwise the electron deficient and this is favored and so this the meta substitution favored on the other hand if you write the para substitution resonance structures on the other hand if it undergoes reaction here and if you write the corresponding resonance structure so it can transform into the product if you see the resonance structure of ok this if you compare the rational structure if the electrophile undergoes a reaction at meta position you see we will have these three resonance structures on the other hand if the electrophile undergoes reaction at para position will have these three resonance structures if you compare these structures here and this is electron with the drawing group if you write this resonance

structures we again the carbocation is comes this carbon this is electron deficient and again is electron deficient this is very less powerful this reaction pathway on the other hand if you write if it undergoes at meta position and always you can look at it and this this carbon is is more electron rich and compared to that therefore this reaction pathway is favored compared to this uh this is the reason why the when you have the electron with the drawing group the electrophilic substitution takes place in meta position not para position this can be understood using these resonance structures let me summarize today we have seen the part to the chemical reaction of carboxylic acids and first we have seen the reaction that involve the cleavage of o h bond and where we have seen the acidity constant and so we have seen some of the reactions and what will happen if you react why carboxylic acid is acidic this we have seen this is because when you form the carboxylate anion that can be stabilized that stabilization comes from the delocalization of p orbital between these two oxygen atoms and the carbon and because of that the carboxylate capacity gas is acidic in nature they can give proton and make carboxylate anion and the acidity constant is measured using pka value the pka value less means is more acidic $pK = -\log K_a$ is the acid dissociation constant and the carboxylic acid weak acids and they are partially dissociated in aqueous medium and we have seen some example therefore when you react acid with base like sodium hydroxide they can react from sodium carboxylate and water is a byproduct you can also react with a weak base like sodium bicarbonate where you generate evolve hydrogen carbon dioxide which we use in the laboratory to identify whether the compound is carboxylic acid or not as soon as you add if it is carboxylic acid it can evolve carbon dioxide and then we have seen some of the reactions where you can cleave the carbon oxygen bond examples are the formation of anhydride if you have the carboxylic acid when you react with the dehydrating agent like phosphorus pentoxide it can dehydrate you can make anhydride which also very important precursor in organic synthesis for various condensation reactions then we have seen esterification and where we can do both acid and base based esterification reactions and this then we have seen how you can convert the carboxylic acid into acid chloride then we can make it more electrophilic in nature and this reaction can be carried out using phosphorus pentachloride thionyl chloride then we have seen

and the transformation of carboxylic acid to amide and this can be done by reacting with ammonia you make ammonium salt when you heat the ammonium salt it can undergo dehydration to give amide and we have seen one example how you can use this method to convert the one to dicaprio benzene digapolic acid to the thalamide then we have seen the reaction where you can convert carboxylic acid into alcohol using reduction reducing agent like lithium aluminum hydride or diborane you can convert a quite efficiently reduce alcohol capacity gas to alcohols and then we have seen decarboxylation reaction when you have carboxylic acid or sodium copper slate when we treat uh with soda lime under heating it can decouple oscillate to give alkanes ah for example if you take for example benzoic acid when you treat with a soda lime you can get benzene um at that end we have seen two types of reactions where the first example involves alba halogenation of carboxylic acid and when we react if your carboxylic acid alba hydrogen atom when we react that carboxylic acid with red phosphorus halogen like bromine chlorine the presence of red phosphorus it can undergo alba halogenation bromination chlorination which can be further converted into different derivatives by with the different nucleophiles for example we have seen how you can replace the br functional group using cyano or voltage or amino functional group you can end up with very useful compounds then we have seen aromatic nitration where if you take benzoic acid and why this nitro group selectively undergoes reactions that meta position not paraposition and is because this coposic acid is known as meta directing group and this can be explained by the writing the resonance structures if the reaction takes place at meta position we can have this kind of resonance structures and you can see here and these are more powerful comparing to that where if you write if it undergoes reaction and para position and what happens you will generate an intermediate carbocation which involves this already have electron withdrawing group and again you will generate carbocation this is not favored therefore this is the reason always and when you do the electrical substitution when your benzene has electron with the drawing group selectively the reaction takes place at the meta position so similarly there are many reactions are known and the bends when you have the benzene ring carboxylic acid can be converted into variety of substituted benzylic benzene carboxylic acids with a

different
electrophile this one of the example with this i conclude thank you very much
you

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