

myself pune murti from de former chemistry iit guwahati i welcome you all to iit fall program in todays class we will study about aromatic hydrocarbons aromatic hydrocarbons that contain at least one aromatic ring and they are also called arrange and for examples So so this is benzene naphthalene andhrasin cyclopentadienyl anion cyclohexatrial cation these are aromatic compounds and they also can be derivatives for example toluene or methyl benzene this is simple benzene and it has substituent one of the hydrogen has been replaced and all these compounds are aromatic compounds if you look at all these compounds they have only carbon and hydrogen atom therefore they are called aromatic hydrocarbons and they can be broadly divided into two groups the compound that contain benzene and its derivatives benzene naphthalene androsine and this one if you look at all these compounds how six membered ring and that they are fused two six-membered rings and three six-membered rings here it has here one of the hydrogen has been replaced by methyl group these compounds are called benzenoids these compounds are called that compound hydrocarbons that contain benzene and the derivatives they are called benzenoids the other compounds they which which are aromatic dowel bond is missing aromatic but they are not they do not have benzene ring these are called benzenoid hydrocarbon aromatic compounds they are called non benzenoids

So aromatic hydrocarbons can be ah classified two groups ah that they contain the benzene and derivatives or the other they are aromatic compounds but they are five membered six membered or seven membered hydrocarbons now let us look at the structure of benzene as taking example

So benzene is a planar molecule as you can see here it has six carbon atoms six hydrogen atoms and they have equal bond length and if you look at the structure

So the bond length is 1.39 armstrong

So all carbon cc bond has same board length and which is 3.1.39 armstrong which is if you compare with carbon carbon single bond which is 1.54 armstrong

So the carbon carbon bond length in benzene is smaller than a carbon-carbon single bond of alkane on the other hand if you compare with carbon-carbon double bond alkene is 1.34 armstrong is slightly longer than alkene carbon carbon double bond and slightly shorter than carbon carbon single bond the bond length of benzene is in between carbon carbon single bond and carbon carbon double bond

So let me draw the molecular orbital structure of benzene you look at it it's each carbon has three sp two hydrogen orbital and two of this orbital this sp2 hybris orbital two of this orbital overlap with neighboring carbon atoms for example in this case this sp2 hydrogen orbital overlap with this sp2 orbital of this carbon to make carbon carbon sigma bond similarly overlapping of this two s p two hybris orbital leads the formation of this carbon karma sigma bond in addition to that each carbon has another sp2 hybris orbital basically it has three sp2 hybris orbital one p orbital with one electron and overlapping of this sp2 hybrid orbital with s orbital of hydrogen generate sigma bond c h sigma bond So this involvement of this sp to hybridization the sigma bond formation makes the benzene ring planar molecule and the bond angle between these two carbon carbon or carbon hydrogen bond is 120 degree they have uniform um a length whether carbon-carbon bond length or c-h bond they have identical bond length and the bond angle between this carbon hydrogen and carbon-carbon bond is 120 degree and this environment as i mentioned just now involvement of this sp2 hybris are we told in the sigma bond formation makes benzene as a planar molecule ah this is the sigma bond formation benzene as you can see here each carbon has three sp two hybris orbital which overlap with the two of this orbital with two carbon atoms one hydrogen atom makes three c h ah three sigma bonds carbon carbon and carbon hydrogen two carbon carbon and one carbon hydrogen sigma bonds now in addition to that each carbon has one p orbital with one electron and let me draw you have the six p orbitals and this orbital parallel to each other and each has one p electron one pi electron each p orbital has one electron and they overlap side on approach to generate So yes and as you can see here a bone below the plane this is your benzene ring and above the below the plane you have the bimolecular orbital

So this is a p orbital the p six p orbital they overlap together to form a pi molecular orbital which has six electrons they are delocalized and above 50 percent of this pi molecular orbitally above the benzene ring and 50 percent of the molecular orbital below the ah benzene ring makes more stable this molecular orbital structure of benzene as you can see here and this involves the sp to hybris orbital the sigma bond formation and in addition to that there is also p orbital which overlap and they generate a bimolecular orbital and above and below the plane as you can see there is a bicloud and makes the

delocalization of these pi electrons makes benzene ring more stable about 36 kilo calories mole<sup>-1</sup> more stable comparing to the simple 1,3,5-hexatriene when you have three carbon carbon double bond if you compare the stability of this one this more stable this because of the delocalization of the pi electrons and as you can see here there is a ring current above and below the plane of the benzene ring this makes the benzene is more stable next resonance and stability just we have seen the structure of benzene and if you look at it it looks single bond double bond single bond double bond single bond but that is not right

So benzene is basically say a hybrid of resonance structures

So these are the two main resonance structure this a hybrid of what is resonance structures different structures but the atoms are the identical position those are called resonance structures and benzene is basically a hybrid of resonance structures can be written like this or this means the electron density is equally distributed in all the carbon carbon atoms and that leads to extra stability of benzene and make the carbon carbon bond length and c-h bond length see uniform the benzene ring

So basically and is a hybrid of resonance structures that makes benzene is more stable another term you have to remember is aromaticity

So your compound to be aromatic and they have to be planar and cyclic a compound to be aromatic hydrocarbon it should be are there are also aromatic high compounds they have heteroatoms a compound to be aromatic they should be planar and cyclic then they should have delocalized pi electrons that's very important d localized pi electrons and third they should have four n plus two pi electrons where n equal to 0 1 2 3 etcetera should be integer see a compound to be aromatic there should be a planar and cyclic they should have a delocalized pi electrons and they should have four n plus two pi electrons the n is can be 0 1 2 3.

So if the compounds satisfy the following then they can be aromatic for examples let us take benzene just we have seen benzene as a planar and just planar molecule it's a cyclic as you can see here and

So it satisfies the first one planar and cyclic d low classify electrons it has a delocalized pi electrons each carbon has one p orbital and if it has one electron all six electrons conjugate delocalized then four n plus two pi electrons you should have four n plus two pi electrons and in this case you have two two six pi electrons you have six pi electrons and four n plus two equal to six electrons and four n equal to four n equal to one

So so in the benzene n equal to one is aromatic now let us take the another molecule So naphthalene see bicyclic aromatic hydrocarbon and if you look at this molecule this also planar and this is a monocyclic that is a bicyclic two benzene ring fused together and anyway cyclic compound that also cyclic and planar molecule and they also have it also has delocalized pi electrons as you can see here and these are conjugally conjugate highly conjugated all carbons you have the double bond single bond double bond is written like this say a conjugated system delocalized by electrons and then let us count it has 10 pi electrons four n plus two equal to ten over n equal to eight n equal to two

So it satisfy all this whatever mentioned here is a planar and cyclic it has delocalized pi electrons it has four n plus two pi electrons therefore is also aromatic now let us these are examples for benzenoids as we have seen the beginning now let us look at non-benzenoid compounds let us take cyclopentadienyl anion the beginning we have seen as aromatic is a cyclopentadiene see the sp<sup>2</sup> to carbon sp<sup>2</sup> to carbon addition to that you have the sp<sup>3</sup> hybridized carbon in between

So when you treat with the base the base can remove this proton

So acidic

So you can generate cyclopentadienyl anion here what happens to this p orbital whatever this p orbital has the lone pair of the electron in this

So this is cyclopentadienyl anion and if you see the orbital structure of this molecule the p orbitals delocalized in this case now whatever the lone pair of electrons is in the p orbital in other words the lone pair is involved the delocalization of this the the cyclo the five-membered ring and make uh this molecule is planar and cyclic reading molecular cyclic and it this lone pair under delocalize with the p orbital of this uh sp<sup>2</sup> hybrid carbon and make the delocalized orbital you can see here this has two electrons this has one electron one electron and one electron volt this is a pi bond this orbital overlap of this orbital gives a pi bond and the lone pair of electron the p orbital overlaps it makes delocalized by electrons right

So if you now see whether it has six electrons or not four n plus two pi electrons and you can see here it has six electrons four are coming from the double bond two comes from the lone pair six electrons you have n equal to one therefore this compound is aromatic and it is not a six benzene but this compound is aromatic and these are called this is called non-benzenoid compound the other example is trapelium cation or cycloheptatrinyl cyclo cation

So this also is not a five of six member ring like benzene but seven membered ring it has six pi electrons in addition to that you have a carbon where a vacant p orbital is there the p orbital in this case is a vacant does not have any electron and this vac and p orbital overlaps with this p orbitals that contain electron pi electrons and makes delocalized molecular orbital see this vacant p orbital overlaps with this p orbitals that contain electron and makes a delocalized ah molecular orbital that make is aromatic and this also cyclic planar and as soon as you form this one then if you count the number of electrons it has six electrons therefore this compound are aromatic now let us look at the normal cluster and isomerism for iupac nomenclature you have to place the name of the substituent prefix to benzene for examples let us look at this molecules and here the methyl group is present at the benzene therefore is called methyl benzene this is called chlorobenzene this is called amino benzene

So when you have more than one substituent for example let us take these two molecules here two bromine atoms are bonded with this benzene here one chlorine and one bromine atoms

So for normal class iu pack nomenclature and we have to when you have more than one substituent then we have to introduce a numbering then we have to place before the uh as prefix before the benzene and for in this case you have uh no problem both or bromine atoms

So we can call at 1 2 dibromobenzene here now there are two different substituents are present and we have to follow the alphabetical order when we numbering and bromo comes fast therefore one then c chloro c comes second therefore this called one bromo two chloro benzene

So when we when the molecule contains two different substituents we have to ah start numbering from alphabetically and in this case b comes fast therefore i have numbered as 1 and chlor then c comes therefore i have number as 2 then we have to place the substituent name before prefix to benzene and then we can get one bromo two chlorobenzene now let us look at the isomerism of substituted benzene let us take dibromobenzene there are three possibilities there in the case of one to dibromobenzene this is just we have seen as one two dibromobenzene this is one comma three dibromobenzene this is

So they have same molecular formula but different structures and in this case the bromine atoms present at carbon one and two therefore is called one two dibromobenzene and is present and at carbon atom one and three one three dibromobenzene and one and four one four dibromobenzene these are called isomers or these called regio isomers and similarly we can see for tribromo benzene

So if you look at these molecules they are also isomers of isomers but they have different structures this called let us compare these three molecules they also have same molecular formula but different different structures these are also called rejoisomers preparation of benzenoids industrial process and first we let us look at it the preparation of benzene and it is derivatives from petroleum when we subject alkanes like that contains c6c8 carbon atoms for example hexane platinum which is supported alumina around 500 to 600 degree celsius and 10 to 15 atmosphere pressure they can undergo cyclization to give cyclohexane the cyclohexane can be further converted into benzene hydrogen

So in petroleum industries whatever the height alkanes are produced that contain c6c carbon atoms can be readily converted into benzene large scale by reacting with platinum which is supported on alumina at high temperature and high pressure to give cyclohexane the cyclohexane can be further converted into benzene by dehydrogenation the other hand instead of hexane and if you have heptane under the same reaction conditions can be converted into methylcyclohexane that can be further transformed into methyl benzene and in case of acting foreign ok this is a one of the large scale process used to make benzene under it is derivatives in petrol from petroleum by cyclization followed by dehydrogenation process the other large scale process is the distillation of coal tar coltar is a mixture of aromatic hydrocarbons benzene naphthalene andhrasin and So on when you distill at a different temperature you produce light oil light oil

contains benzene and xylene and

So on you when you distill cold tar and you get the light oil that when you wash with the acid to remove the base then base to remove the acid then final distillation can produce benzene and toluene and xylene and

So on this is one of the another process used to make benzene and industry process is distillation of coal tar in addition to that there are also methods available to make benzene and its derivatives the laboratory scale the first method is treatment of benzylic or substituted benzene carboxylic acid with a soda lime when you react benzoic acid with soda lime and carboxylic acid will be converted into benzene and sodium carbonate this process used in the laboratory the other process is reaction of alkynes for example three molecule of ethane when you pass combine together when we pass through red iron hot to give benzene this ah three molecule can combine together under this reaction conditions to give benzene this another method used to make benzene the third approach is if phenol is available when we treat phenol with zinc dust and it can undergo reaction to give benzene and zinc oxide

So these are the three common methods are used to make benzene in the laboratory for industrial process just we have seen from petroleum industry petroleum industries and we can produce a lot of  $C_6H_6$  alkenes that can be readily reacted with the platinum catalyst which is supported alumina at high temperature pressure it they can be converted into the corresponding benzene derivatives and the another approach industry uses to make benzene is distillation of coal tar at different temperatures at below 200 degree celsius and that is called light oil that can be distilled out from coal tar that can be further treated with acid followed by base then water and we will end up with mixture of benzene and methyl benzene and

So on that can be further distilled to get pure benzene and methyl benzene compounds now let us look at the physical properties of benzene physical properties

So aromatic hydrocarbons benzene and the derivatives are non polar compound

So they are usually solid or liquids they are liquids and solids they are well soluble in organic solvent and insoluble in water aromatic compounds ah exhibits strong odor and the vapors of aromatic hydrocarbons are toxic in nature in summary

So in this class we have seen ah part of aromatic hydrocarbons first we have seen ah the structure and bonding of benzene then we have seen the resonance and the stability of benzene then aromaticity the nomenclature and isomerism and preparation of benzene at the end of the lecture we have seen the physical properties of benzene with this i conclude the next lecture we will see about the reactivity of benzene you