

myself punya murthy from department chemistry iit guwahati i welcome you to iit paul program in this class we will study about alkanes the last class we have seen about the structure and bonding isomerism nomenclature of alkanes and in this class we will study about physical properties chemical properties and conformational analysis of alkanes the first four member of alkenes methane ethane propane butane they are gases the next 13 members  $C_{12}$  to  $C_{17}$  alkenes that contain  $C_{52}$   $C_{7}$  in carbons they are liquids and carb alkanes that contain 18 or more than 18 carbon atoms wax like solids

So the first four member of this family a series is gas they are at room temperature and the next 13 alkenes see phyt car alkenes that contain  $C_5$  to  $C_7$  carbon atoms they are liquids and alkanes that contain more than  $C_{18}$  carbon atoms they are solids

So if you look at ah for example ethane or any alkane

So the electronegativity of carbon is 2.6 and hydrogen is 2.1

So is non polar strong and this also almost non polar and strong

So alkanes are almost non-volar compounds they dissolve only in non-polar sound like benzene carbon tetrachloride they are insoluble in water

So alkenes are hydrophobic in nature they are soluble only non polar solvents and insoluble in polar solvent like water

So if you go for boiling points let us take compare butane and pentane hexane let us compare the boiling point of this linear alkanes this just we have seen this is at room temperature is gas  $0^\circ$  degree boiling point of this is  $0^\circ$  degree this is  $36^\circ$  degree

centigrade the boiling point of this one hexane is about  $68^\circ$  degree  $68.7^\circ$  degree celsius

So if you increase the molecular weight if the alkanes are linear increase the molecular weight if you comparing this has a four carbon atom this has five carbon atoms we increase of 15 right carbon 12 and 3 15 increase the molecular weight the boiling point increases and if we increase further in this next comolog series one more carbon atom the boiling point increases to  $68.7^\circ$  degree celsius therefore the boiling point increases with increase of molecular weight this is because the intermolecular forces between the alkanes increases when you increase the molecular weight the surface area is more and this ah because of van der waals forces between uh the molecules increases when you have the longer chain and they have more surface area now if let us compare the if you have the linear alkanes if you increase the molecular weight the boiling point increases now let us compare the boiling points between isomers let us take this pentane

So the linear one has  $30^\circ$  degree celsius and the other two isomers this is two methyl butane the other one is this is two comma two dimethyl propane if you compare the boiling point and this is this this about this boiling point of this is  $28^\circ$  degree celsius uh this one is  $9.5^\circ$  degree celsius

So you compare this all our iso structural isomers of pentane this is a linear one is a branched one you have one substituent in this case then the boiling point decreases to  $28^\circ$  degrees celsius  $36$  to  $28$  over degrees is  $8^\circ$  degree celsius when you increase the branches this is it has two methyl group substituent and in this case the boiling point for the decreases to  $9.5$  this is because the molecule is now compact smaller in size comparing to that the surface area is reduced if the intermolecular forces decreases in this case that is responsible when you have branches the boiling point degrades that compa when you compare with the linear alkanes

So just we have seen the physical properties of alkanes where we have seen the whether they are gas or solid liquid at room temperature and then ah non-polar character of alkanes then we have seen the boiling points they are also colorless and waterless now let us go for the chemical properties of alkanes and just i have shown you and the electronegativity difference between carbon and hydrogen is very less they are almost nonpolar molecules and

So the electron distribution between this carbon carbon equally distributed the two electrons the bonding electrons is equally distributed between these two carbon atoms therefore is right and similarly here also this almost nonpolar the electron density between this hydrogen carbon is equally distributed therefore the polar reagent cannot react at normal temperature room temperature they do not react in other words do not react with acid base oxidizing reduce agent because of the non-polar character as well as the strong bonding between the carbon carbon carbon hydrogen however under a high temperature and they can undergo some kind of chemical reactions we are going to discuss those reactions next and they can undergo two types of reactions one is substitution reactions the another one is thermal and catalytic reactions

So we will see two types of reactions thermal means when you heat burn the high

temperature they can undergo degradation we will see some of the which are very useful uh reactions and also there are some reactions when we use catalyst then they can undergo reactions first let us see the substitution reactions

So when you have alkane for example methane you can replace the hydrogen with the for example halogen nitro group sulfonyl group halogen it can be fluorine chlorine or bromine or iodine you can replace one of the hydrogen with halogen or you can also introduce you can replace with nitro group and sulfonyl group

So this is called substitution reactions let us take

So these reactions are effective at high temperature about 500 more than 500 degree celsius ah let us take the halogenation reactions example try to understand mechanism of this reaction when you uh treat a methane with for example halogen let us take chlorine at higher temperature above 500 degree celsius or uv light when exposed to uv light or higher temperature they can convert into chloromethane and hcl this can also can undergo further reaction with the chlorine and it can get a dichloromethane then trichloromethane tetrachloromethane in basically you will end up with mixture of compounds chlorinated compounds when you heat at high temperature or iv visible light is an example for substitution reaction what happens here one of the hydrogen is replaced by the chlorine substitution and we generate hcls by product if you compare the reactivity of halogens with methane and this is a reactivity order of fluorine is very reactive then chlorine then bromine then iodine

So if you if you compare the reactivity of hydrogen this is a primary hydrogen methane and it can also have uh tertiary secondary hydrogen atoms and tertiary hydrogen is more reactive compared to the primary primary secondary secondary is more reactive comparing to the primary hydrogen atoms this is a reactivity order of halogens towards alkane and this is the reactivity or order of hydrogens towards a halogen if primary tertiary hydrogen it will more reactive compared to secondary secondary is more reactive comparing to the primary hydrogen atoms and if you compare this reaction of with the fluorine is very very reactive very difficult to control very reactive but chlorine we can control of course you will end up with mixture of compounds and bromine is very slow when you go for iodine and you can react but the reaction is reversible and before going to that let us see the mechanism of this reaction then we will see the iodine reaction

So mechanism it involves three steps first what happens the chlorine this is called initiation step the chlorine undergoes homolysis when you ah expose to light or heat even light and we generate chlorine radical is a free it involves a free radical process ah this chlorine chlorine bond can under homolysis generate two chlorine radical this called initiation step once if you form the chlorine radical the chlorine radical can react with the c-h bond and this is called propagation step and the chlorine radical now you have the c h three

So now the chlorine radical can react with the c h bond

So you you will end up with c h three dot plus hc

So chlorine radical reacts with ah methane uh you produce now methyl radical and hcl

So this methyl radical can react with chlorine you will generate chloromethane and cl dot

So the methyl radical can react with chlorine you produce chloromethane and chlorine radical these two steps this and this will go on until you have the reactant in your past this called this step this and this can repeat and go on like this and you'll produce until you have the reactant once the reactant is consumed and what can happen these two radical can combine together can generate a neutral molecule for example this called termination step

So you have that chlorine radical this two chlorine radical can combine together you generate again cl<sub>2</sub> chlorine methyl radical you have two methyl radical current combined together you can generate ethane or chlorine radical you have this can react with melting methyl radical you generate

So this is called termination step basically free radical in reaction involves three steps chain initiation where you generate your radical now of course different methods are available you can use a light heat and peroxides like to initiate the reactions once you form the radical this radical can react with your substrate alkane and you generate alkyl radical the alkyl radical further react with your halogen and generate corresponding alkyl halide

So once the alkane is consumed the free radical can combine together and then you generate covalent molecules this is about the mechanism of the halogenation of alkanes So in just we have seen uh the formation of chloromethane the chloromethane also can

further react with the halogen you get similar way dichloromethane trichloromethane and tetrachloromethane basically you will end up with mixture of halogenated alkanes and i mentioned that the i when you react with iodine the reaction is reversible to push forward the reaction what we can do when we add extra oxidizing agent in this reaction for example  $\text{HI}$

So this can be now converted into  $\text{I}_2$  and water

So when you add this oxidizing agent the reaction can be carried out the iodination can be carried out if you do not add the oxidizing agent and the reaction is reversible and the reaction can stop as you can see here however when you add this one the reaction can be perceived you get the iodine methane

So far we have seen the halogenation of alkanes now let us go for the next reaction oxidation they can be broadly divided into two groups computing in this what happens when you ignite for example methane it be converted into within the presence of excess oxygen it can be converted into carbon dioxide water plus heat

So when you ignite alkene the excess of oxygen you generate carbon dioxide flame and water is a by-product you produce heat

So this is the basis of uh what we use alkanes is fuel and you can generate lot of heat for production of power and we burn when you ignite alkenes and you can produce a lot of heat and the general equation for the computation reaction is  $\text{C}_n\text{H}_{2n} + \frac{3n+1}{2}\text{O}_2 \rightarrow n\text{CO}_2 + (n+1)\text{H}_2\text{O} + \text{heat}$  this is the general equation used for computation reaction in this case methane is carbon is one and one and four pi two and this is going to be oxygen and this is a equation and in this case is going to be two oxygen and carbon dioxide is going to be one and the n plus one and two molecular water and they produce heat

So this this case completely uh the alkanes uh ignited and if you do not have sufficient oxygen and if you have less amount of oxygen and the reaction stops and you produce carbon and water

So if you do not have sufficient amount of oxygen and the reaction stops and produces carbon and water and the carbon we use for various applications for filtration as well as for making ink and for cottages next partial oxidation and in the process of catalyst and alkanes can be oxidized to for example methane can be oxidized the presence of molybdenum oxide can be oxidized to aldehyde formaldehyde is partial oxidation or controlled oxidation

So alkane can be oxidized to formaldehyde similarly if you have ethane ethane can be oxidized the presence of manganese are state to acetic acid or ethanoic acid it can be oxidized these are called control oxidation

So alkanes also can be oxidized there are now

So many uh modern methods is available to oxidize alkene to alcohols aldehydes carboxylic acids the next reaction is isomerization

So for example ah butane when you treat a linear alkanes with aluminum anhydrous aluminium chloride the process of hcl gas they can undergo isomerization to give two methyl propane this reaction can be carried out at room temperature

So when you treat n alkanes with anhydrous aluminum chloride in the process of hcl gas they can undergo isomerization to produce branched alkanes this is called isomerization reactions of course we get mixture of compounds this is the major product and similarly instead of butane when you react with pentane a

So you will get two methyl butane plus two comma two dimethyl propane you will get mixture of more compounds these are two major compounds and basically the alkanes can undergo isomerization to give two methyl butane and two two dimethyl propane and other byproducts

So these are called isomerization reactions this reaction can be easily performed using as i mentioned earlier using anhydrous aluminum chloride and dry hcl gas the next reaction is aromatization or forming reactions n alkenes having more than six carbon atoms when you treat the alkane at higher temperature and pressure and they can undergo cyclization followed by dehydrogenation to give aromatic compounds for example when you react n-hexane at high temperature around 700 degree celsius when you heat at high temperature in the presence of in under 10 to 15 atmosphere pressure the presence of for example chromium trioxide alumina catalyst and it can undergo dehydrator dehydration followed by cyclization to give benzene in this case a hydrogen gas similarly instead of hexane if you have heptane you can make television if you have octane you can make ethyl benzene and

So on using different catalyst this called aromatization reaction the next example is a reaction with the steam when you react alkane in the absence of air at higher temperature the price of nickel catalyst for example methane when you heat at higher temperature the price of nickel about 1000 degree celsius higher temperature they can convert into if you do not have the options of air they can convert into carbon monoxide plus hydrogen gas

So this is the process industry you use to make hydrogen gas

So the reaction here when you treat alkane when you treat alkaline with the steam at higher temperature the preserved catalyst and the options of air that is very important you produce carbon monoxide and hydrogen gas this is industry used to prepare hydrogen molecules hydrogen gas the next reaction is pyrolysis of alkanes is also cr is called cracking and higher alkenes can be ah cleavage into smaller molecules which can find broad utilities as fuels and for other applications for example let us take ethane when you heat ethane at higher temperature at 500 degree celsius the options of air it can undergo pyrolysis to give ethylene methane hydrogen gas

So when you heat at higher temperature the options of air it can undergo cleavage to give a mixture of ethylene methane in this case hydrogen gas

So this reaction takes place via free radical pathway what happens uh as we have seen the case of chlorination this also involves three steps initiation step

So the ethane can undergo homolysis to give two methyl radical under heating at 500 degree or higher temperature you generate two methyl radical this is the initiation step once you form this one the methyl radical can react with another molecule of ethane can generate methane plus ethyl radical first the ethane under hose homolysis at higher temperature to give two methyl radical this methyl radical now reacts with the ch bond of this ethane you generate methane plus ethyl radical this is called propagation step this institution step where you generate the radicals once you form the ethyl radical this ethyl radical can undergo cleavage as shown here to give ethylene a carbon carbon double bond plus hydrogen radical this hydrogen radical now react with ethane you produce h two plus ethyl radical this can go on ah like this repetition of these steps this is called the provocation of the reaction

So this radical two radicals also can combine once as i mentioned earlier once the substrate is consumed

So these two radical can combine together the reaction can be stopped this called the termination reaction termination step

So the two hydrogen radical combined together h you get hydrogen molecule and similarly two ethyl radical can combine together higher alkene of course this can undergo further reaction and it can be converted into ethylene and methyl

So basically what happens in this case and the overall if you look at the reaction i wrote the ethane can be converted into ethylene methane hydrogen gas you can see here how the methane forms how the ethylene bonds how the hydrogen bombs

So this this very important process for example let us go for the other example dodecane So dotakin is a main component of kerosene when you heat dough taken in the presence of platinum palladium nickel catalyst at around 700 degrees celsius they can undergo cleavage to give a mixture of heptane and pentane smaller fractions ah other hydrocarbons

So this is called cracking of hydrocarbons this is very important process to make fuels now let us see the confirmation analysis of alkanes in alkanes the carbon carbon single bond can undergo rotation that can give a different spatial arrangement of atoms in space that is called conformational isomers for example let us start with ethane

So this ethane and if you look look at from this side we can see here this carbons bonded with three hydrogen atoms and behind the next carbon also is bonded with three hydrogen atoms say exactly behind this one you can see from here and this can have one structure and due to the ah single bond rotation this can undergo single bond rotation you can have a spatial arrange different spatial arrangement of atoms and you can have here in this if you look at from this side you have the ch bond in between this uh two ch bonds and if you compare these two in this case the ch bond just behind to that and here the c h bond is in between these two ch bonds due to the carbon-carbon single bond rotation these two are called conformers or automates and or conformational isomers

So let me draw the sawhearts and human projections of ethane this is sahar's projection So the whatever the structure i show you is this one look at it this one if you look from this side and this hydrogen is exactly behind to that and this is called eclipse conformation and this one if you look at it this due to rotations of this group there is a different spatial arrangement of these atoms in space and this is a extreme case and

this is called staggered stacked confirmation this is the sahar's projection of ethane this is a human projection of

So this is the front side carbon this is the rear carbon and you can look at it this one this is the for eclipse conformation is a staggered conformation these two are called conformational isomers or different conformations and if you look this one look at this one this is just behind that there is a repulsion between this bond bear this bond bear So therefore this conformer has more energy potential energy comparing to that in other words this is less stable about 2.8 kilo calories per mole

So due to the repulsion between these two bond pairs and it has more energy potential energy comparing to that in this case and

So this c h bond is in between these two one this there is a less interaction between the bond pairs if if you compare this eclipse confirmation and this exactly you can

So here you can see here also this is the eclipse confirmation this is stacked confirmation and the difference between these two

So he is for example in this case this got dihedral angle these two are extreme cases right this is the more sterically hindered one and this due to the bond repression but this is called torsional strain

So due to the bond repulsion and it has more potential energy and if you compare the other one this extreme case this has is more stable one and compared to that these two are extreme cases in between there are

So many infinite confirmations available and these are those are called skew conformations for example here the dihedral angle is  $0$  here the dihedral length is maybe 5 5 to 10 right this is this is called skew conformation in between this extreme case this exclusive one extreme case this is the staggered one is more stable less stable in between whatever the confirmations are available there are called skew conformations now let us see the energy level diagram and if you see look at it this one and

So that room temperature due to collision and that they get potential energy about 15 to 20 kilo calories per mole

So there is no problem

So room temperature they can readily undergo because the energy difference between these two conformations is about only 2.8 kilo carriers they can readily undergo rotation to have infinity number of conformations and if you look at the energy level diagram of two of these two extreme confirmations

So potential energy rotation

So this is the energy level of the staggered confirmation of ethane this is a staggered confirmation this is the eclipse confirmation this again staggered confirmation

So in between whatever the energies this the gap between these two is about two point eight kilo calories per mole in other words this stacked confirmation about two point eight kilo color is more stable comparing to this and whatever the confirmations we have in between those are called skew conformations for example this one

So so let us summarize now and

So alkanes can readily undergo carbon-carbon single bond free rotation that can lead to the different spatial arrangement of atoms in space and those are called conformational isomers or conformers or tumors and if you compare these two if you take ethane and these are the two extreme conformations this is the less stable due to the torsional strain and this is the more stable and in between there are

So many confirmations possible and those are called skew conformation and when you you can go on like this for if you want this e about ethane if you go for propane and this will be the eclipse conformation and this will be the staggered confirmation for propane and for butane this will be the staggered confirmation and there are this will be the this and these two will be the eclipse confirmation these are less stable comparing to this you can go on like this let us summarize today we have seen the physical properties of alkanes then we have seen the chemical properties where we have seen the ah

substitution reaction um then thermal and catalytic reactions where we have seen oxidation reactions complete oxidation of alkane to carbon dioxide and water where we generate a lot of heat which is the basic and fundamental process for using hydrocarbons as a fuel then we also we seen fossil oxidation reactions uh the prison of catalyst at appropriate temperature the alkane can be oxidized to aldehyde or alcohols then we have seen isomerization reactions and alkanes linear alkanes can be converted into branched alkanes isomers using anhydrous aluminum chloride the presence of dry hcl gas then we have seen aromatization reactions when you have linear alkanes that contains more than c

six carbon atoms they when you treat uh these alkanes at high temperature under pressure with catalyst like chromium trioxide supported alumina they can undergo dehydrogenation followed by cyclization to give aromatic compounds then we have seen the reaction with the steam where what you can do in the absence of air and the prism nickel catalyst alkanes can be converted into carbon monoxide and hydrogen gas this industrial process we use to generate hydrogen gas then we have seen pyrolysis very important reaction the higher hydrocarbons can be cracked into smaller molecules that we use as fuels and we have seen one example for example how you can convert ethane into ethylene and methane and hydrogen gas and this reaction uh involves free radical pathway and then we have seen one example how the main component of kerosene do decay dotakin can be converted into heptane and pentane and other smaller fractions is in the presence of palladium platinum based catalyst at higher temperature

So these reactions are performed in the absence of air and then we have seen the conformation analysis where due to the carbon carbon single bond rotation and the atoms can be arranged a different way in space these are called conformational isomers or conformers rotomers and this they have infinite number of confirmations but if you go for extreme and in the case of ethylene ethane we have seen we can have two conformations one is uh eclipse conformation another one is stacked confirmation these two are extreme cases and the energy difference between them is 2.8 close kilo calories per mole and So ah

So this the in the case of eclipse conformation is less stable due to the torsional strain and there is a repulsion between the bonding electrons and they have less 2.8 kilo calories more energy than the stockard conformation and in between what are the confirmations available they are called skew conformations we have seen two projections uh one is uh stackard known as sawhorse and newman projections similarly we can also go on for other alkenes like propane and butane So with this i conclude this lecture thank you very much you