hello let us continue with the fundamental concepts in organic chemistry the basic principles that are used in organic chemistry in the last lecture we were looking at the electronic effects in organic chemistry in the electronic effects there are four types of effects we already considered the inductive effect and the electromagnetic effect with suitable examples we have seen this this is a permanent effect this is a temporary effect this is observed only during the course of the attacking reagent approaching the substrate molecule undergoing a particular reaction for example the third effect is what is known as a resonance effect or effect the resonance effect is a very important effect in organic chemistry and this is also a permanent effect depending upon what kind of groups are attached you can classify the groups into electron donating groups which will have plus or effect in other words a positive resonance effect you can have electron withdrawing groups which will have minus r effect or negative resonance effect now what is resonance resonance is essentially delocalization of electrons particularly of the pi electrons without changing relative positions of the atoms in other words you are not allowed to move the atoms around the atoms stay in the same place whereas the electrons can move from one position to another position in other words you can delocalize the electron density around the molecule

So this is a very important concept namely delocalization of electron let us illustrate it with a simple example of a carbonyl functional group now what would be a resonance structure of the carbonyl functional group remember there are two lone pairs of electrons on the carbon the pi bond in the carbonyl functional group is more mobile than the sigma bond

So it is possible to delocalize the pi electron if you were to delocalize the pi electron in this particular fashion this would correspond to the resonance structure of the carbonyl functional group one can also try to delocalize the electron from here to here where the charge reversal takes place for example now this is a neutral structure and these are the delocalized charged structures of let us say carbonyl functional group now important role in doing the delocalization business in the resonance structures is that you cannot violate the octet rule now if you look at these two structures the lewis structures that are drawn here if you look at carefully because of the electronegativity difference between oxygen and carbon you have a valid reason to delocalize the electron onto the oxygen because oxygen is more electronegative in doing

So you are also not violating any kind of an octet rule this is octet all right this is extract but with the carbonium ion

So it is all right

So one cannot violate the octet rule but if you look at this particular structure the carbon has 10 electron around it if you look at the lewis structure of the carbon itself and it bears a negative charge also

So this is not a valid structure at all for the resonance structure and this is the only valid structure resonance structure for the carbonyl functional group

So i hope this is illustrating the essence of the we are not changing the positions of atom in any of these things the relative positions or atoms are essentially same we are only delocalizing the pi electron to develop charges and as a result of that you have a concept of resonance coming into picture certain compounds a fixed lewis structure alone cannot explain the property of the compound i will illustrate this with this example when a carboxylic acid ionizes to give a carboxylate the carboxylate ion is written like this normally this is how you write the carboxylate ion and this would be the lewis structure of the carboxylation there are three lone pairs of electron on the oxygen bearing the negative charge and two lone pairs of electron on the oxygen bearing the no charge now if you look at the carboxylate ion this is a single bond and this is a double bond

So the bond length here should be different from the bond length here however spectroscopic evidences show that the two bonds are of the same length both spectroscopic evidences as well as x-ray crystallographic evidences where you can actually measure the bond lengths there is no difference between this carbon oxygen bond and this carbon oxygen bond

So this structure alone cannot explained why the bond distances of the carbon lengths of the carbon oxygen bond should be same because this would indicate these two band lengths should be different however if you invoke the concept of resonance and delocalize the structure like this then you can understand why the bond lengths become simple

So a structure where the two canonical representations are given each one has a single bond double bond character but neither of the structure explains the equal bond length of carbon oxygen bond

So the structure should be somewhere something like this for example where the negative charge is essentially delocalized on both the oxygens equally and this would be the hybrid structure hybrid of structure 1 and structure 2 essentially if we equally delocalize the negative charge on both the oxygen then the probability that this carbon oxygen bond and this carbon oxygen bond will be equal in nature

So this is an example of a resonance structure of this particular molecule similarly there are several examples that one can give for the resonance structure this is a alpha beta unsaturated ketone once again because of the electronegativity difference between the carbons and oxygen one can delocalize the charge onto the because the electron movement is towards the more electronegative oxygen this carbon acquires a positive charge and the oxygen acquires a negative charge for example

So this would be a resonance structure of the alpha beta unsaturated molecule

So the concept of resonance is extremely important one other example that i can show is with respect to benzene benzene is a very classical example of a molecule which shows resonance structures most of the benzene and benzene derivatives do have the resonance effect in this particular manner let us take the example of benzene the resonance structure proposed by calculate is an alternating double bond structure like this

So benzene structure cannot be represented by either of these structures either of the structures suggest that there is an alternating double bond and single bond but now we know from spectroscopy as well as from hexa crystal structures all the six carbon carbon bonds are equal length that is the reason the benzene structure is best represented by either a circle around the six carbon indicating that this is a completely delocalized system how do you delocalize it by pushing the pi bonds around the ring system like this remember we are touching only the pi bonds and not the sigma bonds in this structure or one can write the benzene structure as dotted line structure like this indicating there is a complete delocalization of the electron around the six carbon in other words the electron density on each one of the carbon will be identical electron density and the bond lengths are identical

So it is highly symmetrical d6h structure symmetry is what we are having highly symmetrical with the six fold axis of symmetry in this molecule now what is a plus or effect and minus or effect as mentioned the functional groups in a molecule can be classified either as the let us consider this particular molecule this is methyl vinyl ether if one were to write the resonance structure of this particular compound one would simply take the lone pair of electron from the oxygen push it on to the carbon here remember the resonance effect here indicates that the lone pair on the oxygen can be donated this is a negatively charged and this is a positively charged system this is very different from the inductive effect you would have written for this compound if you have to write the inductive effect oxygen is more electronegative than carbon

So the inductive effect is going to be operating in this one

So oxygen is a minus i effect because of the fact that it is more electronegative than carbon but the lone pair on the oxygen can be delocalized onto the pi bond which is in conjugation in other words this phenomenon is known as conjugation in other words the orbital bearing the lone pair of electron on the oxygen and the pi orbitals can interact with each other and thereby the electron density can be delocalized onto this carbon bearing a negative charge in this particular position oxygens bear the positive charge this kind of an effect is known as the plus or effect positively inductive effect suppose the same vinyl group is conjugated to a carbonyl functional group for example now you will have exactly the opposite effect this is a easily delocalizable system and

So is this easily delocalizable

So the delocalized structure is going to have negative charge on the oxygen and the positive charge on the carbon it is exactly reverse of what we did earlier this will be the minus r effect please remember in all these structures between the two structures neither of these structures do have a permanent existence to explain the reactivity of the molecule it is the hybrid structure between these two structures is what is going to explain the reactivity of the organic compound that you have for example if the question is asked if this molecule were to react with the proton where will it react it can react here the lone pair can be protonated it can react here also because it is partially electron density according to this resonance structure is high this is a completely octet obeyed resonance structure

So it is a valid resonance structure

So the protonation can also take place here in fact vinyl ethers undergo protonation the double bond the terminal carbon of the vinyl group for example resonance structures where the canonical structures are represented they are represented by a double headed arrow unlike an equilibrium arrow which is a two side arrow for example let us say for example this is the resonance structure this is represented by a double headed arrow like this and not by an arrow like this which is reversible arrow one cannot use a reversible arrow to represent the the important point that one needs to remember for writing the resonance structure is one lone pairs and pi electrons can be delocalized and not the sigma electrons in a molecule secondly these resonance contributing structures are represented by an arrow which is a double headed arrow thirdly no positional no change in the relative positions of atoms in other words you cannot break sigma bonds in a resonant structure that is what essentially means if you break a sigma bond the position of atoms will change quite dramatically

So there is no change in the position of the atoms fourth point is the canonical structures are non-existent in other words the individual structures are non existent it is the hybrid structure which represents the overall structure of the reactivity the hybrid structure is representative of the true nature of the molecule oftentimes one cannot write the hybrid structure properly like in the case of benzene for example you draw it with a circle or with the dotted line as the case may be now let us look into some more examples of the resonance effect of the plus r i plus i sorry plus r and minus are effects in aromatic system let us take the example of aniline now aniline the nitrogen has a lone pair of electron

So one can write the the pi electron density around benzene is for example in this particular measure donut shaped pi electron density on the top as well as in the bottom of the molecule if the nitrogen lone pair also in the same plane as the plane of the benzene ring for example the plane of the pi electrons in the benzene ring for example then there is a possibility of interaction between the pi electron of the benzene and the lone pair of electron of the nitrogen one of the principle requirement for delocalization of the electron is the orbitals have to be in the same plane if the orbitals are in the same plane it facilitates the lateral overlap and thereby delocalization can be written

So one can write the delocalization of electron in this particular manner you are not violating any octet structure here please follow that rule also carefully

So fifth point here is octet rule not violated

So this is one of the resonance structures of aniline one can also delocalize this structure in this particular manner we can proceed further to delocalize this manner for example

So these are resonance canonical structures of aniline what it tells us is essentially the electron densities in these positions namely the ortho position and the paraposition of the aniline ring have higher electron density compared to the meta position because if we look at all these structures the negative charge or the higher electron density is present in the orthocarbons and in the para carbon but not in the meta carbon you do not have a delocalized structure with the meta carbon having a negative charge

So from the resonance structure we conclude that aniline has higher electron density in ortho and para positions ortho and para positions this would mean that any electrophile or an electron deficient species will react with aniline in the ortho and para position that would explain the reactivity of aniline to undergo substitution reaction in the ortho and para position which we will see little later

So the effect that is shown in the case of aniline would correspond to a plus or effect because it is a positive reinforcement of electron onto the ring corresponding to that particular structure

So this is an example of plus or effect let us take an example of a minus r effect for this you need to have a electron withdrawing functional group let me take the famous nitro functional group as the electron withdrawing functional group this particular manner the oxygen has the necessary number of lone pairs of electron for example to represent this structure the nitro group itself can undergo the resonance structure in this particular manner this is within the nitro group of the nitro benzene without violating any octet rule for example we have drawn this particular structure one can also for example because of the electron withdrawing nature of the nitro functional group delocalize the pi electron from the aromatic ring on to the nitro functional group this can also be done

So that particular structure if you follow the arrow which is indicated by the red chalk here the delocalization of the pi electron from the ring essentially creates a positive charge on the ring and the negative charge on the oxygen because oxygen is electron withdrawing or the nitro group is electron withdrawing group here the nitrogen is electron donating one can proceed further with the delocalization and move around the electron further down like this

So these are all canonical structures of the or the resonance structures of the nitro benzene nitro benzene if you want to describe fully the electronic effects this is electron withdrawing by both inductive effect

So it is a minus i effect as well as minus r effect it has that is why it is one of the powerful electron withdrawing functional group is in organic chemistry on the other hand if you want to describe the electronic nature of the aniline itself it is inductively electron withdrawing because of the difference in the electronegativity effect

So it is a minus i and plus r effecting group is what the amino functional group is

So one can based on this example one can illustrate the point of resonance effect by means of aniline as an example for the plus r effect and nitro benzene as an example for the minus r effect the next electronic effect is known as the hyper conjugation effect hyper conjugative effect here again a c h bond that is attached to a unsaturated system either a double bond or a triple bond undergoes delocalization of electron let us say for example this is the pi orbital of the ethylene unit suppose if there is a carbon that is attached with the hydrogen that is present here if the carbon hydrogen bond and the pi bond is coplanar then one can draw the orbital of the sigma orbital of the c h can be drawn like this one s electron overlapping with the here this is an s p three hybridized carbon a methyl group is what we are representing in other words structurally this would correspond to c h three c h double bond c h two a propene molecule is what we are referring to as the system here if these three orbitals come to coplinarity then there is a possibility of delocalization of electron of the sigma bond delocalized onto pi orbital and this is a kind of effect which is known as the sigma resonance effect and this is also known as the hyper conjugative effect in other words this is conjugation this bond is in conjugation with the pi bond and as a result of that the structure that one normally writes is as if the electron density from the carbon hydrogen bond is completely donated onto the vinylic group representing this particular structure like this and this is what is known as a high there is no complete breaking of the carbon hydrogen bond but the traditionally it is the hyper conjugative effect is represented as if there is an ionization of the carbon hydrogen in fact there is no ionization of the carbon hydrogen bond this is only a canonical structure that is represented by the charged separated structure like this please remember one of the cardinal rule of delocalization is that you do not break the carbon carbon bond or a carbon hydrogen bond which is a sigma bond

So this is not completely broken there is a delocalization of the electron density from the sigma orbital of the c h bond onto the pi bond and that is known as the hyper conjugative effect hyper conjugative effect essentially explains the stability of thermodynamic stability of for example this one compared to this one a fully substituted double bond is more stable thermodynamically compared to an unsubstituted double bond like this here there are no groups which can lend hyper conjugation effect in the case of ethylene whereas here there are 12 hydrogens which can participate in hyper conjugation effect

So as you go from the tetra substituted to try substituted to di substituted to mono substituted alkenes the thermodynamic stability goes down in the series this is thermodynamically most stable one of the explanation that is given is that it has 12 hydrogens which can hyper conjugate and stabilize the delocalize the sigma electron onto the pi orbital thereby imparting stability towards the overall effect hyper conjugation effect is also responsible for explanation of the stability of carbonium ions suppose if it is a carbonium ion center carbonium ion is having a empty p orbital by virtue of a positive charge associated with this one

So the adjacent carbon hydrogen sigma bond can essentially participate in delocalization of electron from the hybridized s p three hybridized c h sigma bond that that electron density essentially get delocalized onto the empty p orbital of the carbonium ion

So if you consider the carbonium ions methyl carbonium ion does not have an alpha ch there is no carbon adjacent to it

So this is the least stable of carbonium ions as compared to for example an ethyl carbonium ion where there are three ch3 there are three ch bonds which can hyper conjugate with the

So essentially what i have written here is c h three c h two plus is what i have written

So three of this hydrogen at at a time one of the hydrogen carbon hydrogen bond can be coplanar with the p orbital empty p orbital

So there are three hydrogens which can hyperconjugate here if you go further to isopropyl cation there are six hydrogen which can hyper conjugate here finally tertiary butyl cation which is this particular cation there are nine hydrogens which can hyper conjugate with this compound the carbonium ion stability essentially because of the hyper conjugation increases in this particular direction the tertiary carbonium ion is more stable than the secondary which is more stable than the primary essentially because of the hyper conjugation effect of the delocalization of a c h sigma bond onto the pi orbital of the carbonium ion m t p orbital of the carbonium ion now let us look at some types of reactions and then proceed further organic reactions can be classified in several categories we will see some of the categories in this particular lecture in the remaining portion of the lecture let us look at types of bond fission now reactions takes place by breaking and making of bonds sigma bonds pi bonds and

So on

So the the mode by which the bonds are broken is important to understand the reaction mechanism of chemical reactions suppose you take a molecule a b there is a pair of electron which is the bonding electron between a and b if it is a sigma bond suppose if the bond breaks in such a manner that they equally share the electron density between the two atoms then it is called homologic band homolytic fission in the homolytic friction one of the electron goes to b the other electron goes to a

So as a result of that a and b now have an odd electron present in them

So it will produce a radical a radical and b radical such a process is known as the homolytic fission a simple example can be seen by taking methyl iodide for example if you shine light on methyl iodide in other words leave it open in the room light it absorbs the energy of the photon and thereby producing a c h three dot and i dot eventually the i dot will go to i two

So it produces the iodine color the c h three dot of course will go to ethylene eight ethane and

So on

So this is an example of a homolytic the pair of electrons that was originally present in the bonding orbital one of them goes to iodine the other one goes to the carbon

So the carbon now is divide of an octet it is having only seven electrons and that is why it is called a radical this is methyl radical is what is represented by this structure the methyl radical has a structure which is represented by having a orbital containing only one electron one can also think of homonuclear diatomic molecules like chlorine and bromine upon photolysis for example or upon strong heating can undergo homolytic bond cleavage to give to chlorine radical or two bromine radicals for example

So these are all some examples of homolytic fission in terms of the bond breaking if you have a paroxy bond as in this case of di benzoyle peroxide this is a homolytic bond cleavage process is possible it can produce a carboxyl radical two carboxyl radicals can be produced from which of course carbon dioxide can go a phenyl radical can be produced in other words a phenyl radical is one where you have five hydrogens on the benzene ring and one of the carbon has a radical which is the phenyl radical that orbital is shown in the form of a dumbbell here and this is a phenyl radical the other hand one can also think about bond diffusion between a and b where based on the electronegativity difference or the polarization of the bond between a and b both the pair of electrons is taken by one of the partners let us say by a itself or b itself in this particular case

So a loses its bonding electron

So it gets a positive charge b gains the additional electrons

So it joins the negative

So you produce ionic species and such efficient is called heterolytic fission heterolytic fission heterolytic fission produces charged species whereas homolytic pressure radical species is what is produced here radicals are formed here ions are formed let us take the example of c h three c c l under suitable conditions the carbon chlorine bond which is already polarized towards the chlorine can be broken and one can produce a ch3 plus and a cl minus more easy to do reaction would be where one produces a tertiary carbonium ion in other words tertiary butyl chloride is even more reactive towards the heterolytic bond cleavage because it can produce a tertiary butyl cation and a chloride ion this kind of reactivity reactions are explained in a nucleophilic substitution reaction as to why tertiary butyl chloride undergoes what is known as a nucleophilic substitution reaction by a unimolecular process compared to a nucleophilic substitution reaction by a biomolecular process by methyl chloride for example

So the kind of bond fission essentially helps understanding the bond fission helps us to understand the chemical reactivity of organic molecules that is why it is important to understand the types of bond fissions that can take place when you study organic reaction what you are essentially studying is to understand the kind of bond breaking and bond making processes that take place in as much detail as possible

So if you take a organic molecule it reacts with some reagent it forms some kind of intermediates finally it forms some kind of a product this is a general scheme that one can give to describe an organic reaction mechanism trying to understand as much as possible the interaction between the reagent and the organic molecule trying to understand as much as possible the structure and the nature of the intermediates that are produced and finally of course the structure of the product one can elucidate by suitable spectroscopic methods and

So on now it is here we need to pay attention these are intermediates which can be free radical in nature

So one can have free radical reaction one can have carbo cation kind of a reaction and can have carbon anion kind of reaction as an intermediate finally one can have carbenes as intermediates now let us take the example of the free radical that we are talking about let us say for example i want to brominate ethane ethane is a saturated molecule it is not a unsaturated molecule in order to brominate it you have to have free radical initiators or you have to have photon h nu essentially means you are shining light on the bromine molecule in that process it produces ethyl bromide and hydrogen bromide as the product how does this reaction take place this is generally explained by the fact that bromine undergoes dissociation in the presence of light to give to bromine radical the bromine radical once it is produced it is a highly reactive intermediate remember it does not have an octet

So it is a free radical free radicals are reactive intermediates

So it abstracts one of the hydrogens of ethylene

So not ethylene ethane producing ethyl radical plus hbr ethyl radical can now react with bromine producing ethyl bromide and regenerate a b r radical the b r radical now again go to another ethylene ethane molecule do a hydrogen abstraction

So this reaction is known as hydrogen abstraction reaction hydrogen abstraction reaction is what is this is a homolytic dissociation

So in the process you produce a alkyl radical alkyl radical stability depends upon the number of hyper conjugative group that is present in the radical system tertiary radicals are more stable than secondary radical which are more stable than primary radical let us have a look at the carbocation kind of a reaction mechanism as i mentioned earlier if you put tertiary butyl alcohol in methanol as a solvent methyl alcohol as a solvent methyl alcohol is a polar solvent it is a hydroxy compound

So it is highly polar in nature under these conditions the carbon chlorine bond undergoes ionization to produce a chloride ion in other words an already polarized carbon chlorine bond is now completely broken in such a manner that the pair of bonding electron is taken away by the chlorine producing a chloride ion in generating a carbonium ion carbocation is what is formed the structure of carbocation is that it is a sp2 hybridized system with an empty p orbital responsible for the positive charge let us say methyl carbocation would be this would be 120 degree in terms of the bond angle it is a planar system

So it is like an sp 2 hybridized carbon for example with an orbital which is an empty orbital containing no electron corresponding to the positive charge that you have in the system

So we have seen what is say free radical and what is a carbocation carbon ions are also reactive intermediates carbanions are generally generated by deprotonation reaction let us take this compound which is nitro methane because of the inductive effect as well as the electron withdrawing nature of the nitro functional group there is inductive effect in all the carbon hydrogen bond also which makes the carbon hydrogen bond an acidic bond in other words the acidity of this carbon is fairly high

So if this is treated with sodium hydroxide for example sodium hydroxide can abstract a hydrogen resulting in the formation of a carbon ion and water the counter ion here will be sodium ion for example the carbon ion of course in this particular case it is stabilized by delocalization on to the nitro functional group one can write resonance structures for example this carbonium ion carbanion which would be this resonance structure

So this is a formation of a carbanion as an intermediate in this particular reaction of course this can further undergo condensation reaction and

So on and

So forth one other example for carbenions preparation is the aldol condensation reaction if we consider acetaldehyde as a substrate the alpha hydrogen of acetaldehyde because of the inductive effect of the carbonyl functional group again the carbon hydrogen bond is acidic in nature if you treat it with sodium hydroxide sodium hydroxide o h minus reacts with the hydrogen producing a carbon ion which is this particular carbonyl methyl carbon ion is a highly reactive substance it is known methyl carbon ion is known as methyl lithium salt methyl magnesium bromide for example they are all examples of carbanion nature of the methyl group the structure of the methyl carbon amion methyl carbanion is pyramidal in nature it is not planar because it has a pair of electron with the ionic charge the structure is pyramidal in nature in other words including the lone pair of electron on the carbon ion it will be a tetrahedral structure if you include this lobe along with these three hydrogens here then it will look like a tetrahedral kind of a structure in this particular case finally let us look at how carbenes are generated carbenes are typically generated by a reaction known as alpha elimination reaction a carbene is a divalent carbon divalent sextet carbon it has only six electrons around it a simplest carbine that you can write is this particular carbene

So if you look at the number of electron around that particular carbene only six electron two electrons of the two hydrogens and two electrons which is on the carbon for example totally six electrons are there it is an incomplete octet system

So it is a highly reactive intermediate in organic chemistry in principle we take chloroform and treat it with a strong alkali not chloroform i am sorry methyl chloride treated with a strong alkali something like 50 percent echo sodium hydroxide or potassium hydroxide this reaction can in fact take place simultaneously both the hydrogen and the chlorine are lost because of the presence of alkali

So hydrogen chloride is eliminated and in the process you end up with ch2 which is a carbene which is a carbene that is produced plus hcl hcl of course is neutralized by the sodium hydroxide on the other hand dichloro carbene can be produced by chloroform reaction of chloroform when chloroform is treated because of the three halogen atoms are attached to the carbon which have the strongest inductive effect in this particular system when it treated with sodium hydroxide it undergoes initially to produce a trichloromethyl radic anion this will of course lose a chloride ion to produce c c l two which is dichloro carbene and a chloride ion this is an example of an alpha elimination because it is a both the groups that are eliminated namely hydrogen first then the chlorine second they are eliminated in a sequence and this is known as the alpha elimination reaction resulting in the formation of the dichloro carbine

So what we have seen in this particular module is the electronic effects particularly of resonance effect and hyper conjugative effect and then we looked at the reactive intermediates which are free radical carbocation carbanion and carbene type of intermediate we will continue in the last model the kind of reactions that organic react types of organic reactions that one can look at and the kind of reaction mechanism that one deals with in organic chemistry thank you for your kind attention you