Technology Enhanced Learning

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Module No. # 01
Lecture No. # 14
Photochemistry AndPericyclic Reactions

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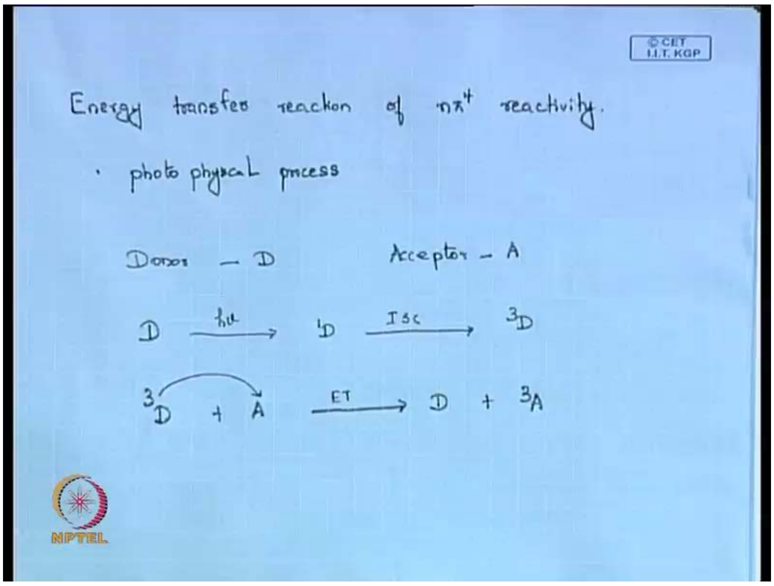

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Energy transfer reaction of $n\pi^*$ reactivity.

- photo physical process

Donor – D   Acceptor – A

$$D \xrightarrow{h\nu} {}^1D \xrightarrow{ISC} {}^3D$$

$${}^3D + A \xrightarrow{ET} D + {}^3A$$

Last class was likereactivity of your n pi star chemistry we covered 3 major reactions 1 was your cleavage reaction another is your hydrogen abstraction and the last few classes we were discussing about addition to pi system so today class what we do is that going to cover the 4 that is your energy transfer reaction and electron transfer reactions so we will start understanding something about your energy transfer reaction of n pi star reactivity so the first thing of energy transfer reaction it is not a basically a photochemical reaction it is a basically a photo physical process it is a so typical photo physical process so what happens is that

Let us consider like a molecule 2 molecules in a system 1 we call as a donor molecules you can call it as band then we will have an another molecule which we will call as an accepter I am talking or and accepter with respective energy 1 can be a donor which can donor the donor another will be a accepter, so what happens is that basically if I take my donor I am not restricting right now to the carbon here I am just taking a donor molecule and then if I shine light it goes to is singlet that is what we studied then it as a chance it undergoes an intersystem crossing and gives you my triplet. See I am not see I have a system in which I have both donor as well as acceptor I am just exciting my donor. I am not doing anything with my acceptor so my donor gets excited with singlet undergoes an intersystem crossing to triplet now this triplet donor react colloids basically colloids with your acceptor and you get a sort of energy transfer. There your donor this is excited triplet energy to your acceptor.

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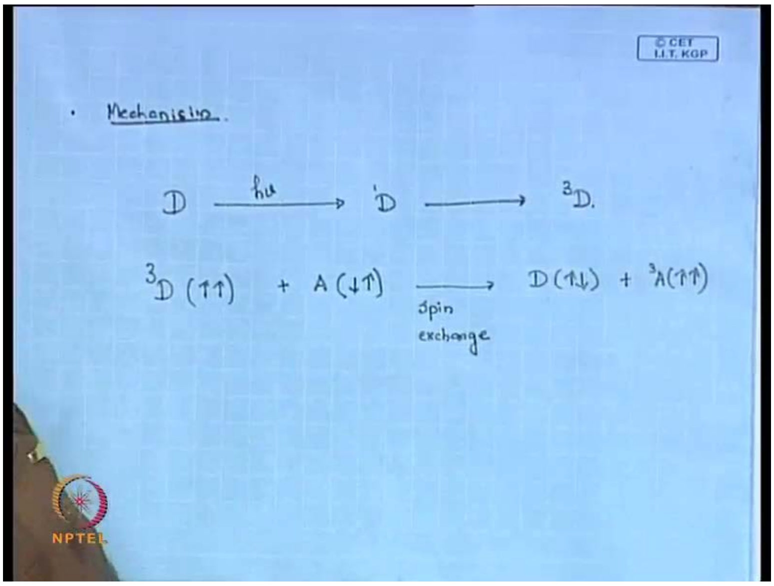

- Mechanism.

$$D \xrightarrow{h\nu} {}^1D \longrightarrow {}^3D.$$

$${}^3D\,(\uparrow\uparrow) + A\,(\downarrow\uparrow) \xrightarrow[\text{exchange}]{\text{spin}} D\,(\uparrow\downarrow) + {}^3A\,(\uparrow\uparrow)$$

So this collusion is between your triplet enactive state of your donor and the ground state of acceptor after the reaction it becomes a ground state donor and a exciter state acceptor see basically I am not shined any light on my acceptor molecule just I have shined light on my donor molecule donor goes to the triplet state and then transfer this energy to the acceptor molecule fine so this process we call as energy transfer reaction now we will see how it happens, you can call as mechanism or how it happens is than call is mechanism of this 1. So as I said I have a donor which gets excited to my singlet then it goes to my triplet.

Now if I say in triplet my donor electron should be looking like this right because this is triplet 2 plus so the electron looks like in this way now I have my acceptor molecule the acceptor is in the ground state so it should be mostly singlet. Now this 2 come and colloid with each other so what happens a type of spin exchange. You can call as an electron exchange or a spin exchange. Basically spin exchange happens between your donor and acceptor, so there will be an exchange of spin so if I right then your donor will be it is you will get a proper spin exchange you can see that donor was initially triplet and accepted was ground state singlet now there was a exchange in spin, were your donor becomes a single t which is in ground state and your acceptor becomes the triplet. So this process this is a type of spin exchange process and it happens because of your electronically stage. That is how this mechanism works energy transfer reaction.

So it is a so what you what are the 2 important criteria’s not criteria what are the 2 important stage it happens is 1 it should happen from the triplet the, second thing is that there should be an spin exchange. The mechanism gives it like this so you should be basically from the triplet and the there should be a spin exchange then you can see the energy of your donor is been transferred to your acceptor. Without exciting your acceptor. You will see how the application what is the beneficial use of knowing why to do the energy transfer reaction, fine so this is the proper mechanism of this. Now we will see like what are the criteria’s for a donor to transfer its energy to acceptor, you cannot take any donor on any acceptor which can transfer so that you excite a donor it will transfer its energy to accept know, there are some criteria’s which donor and acceptor should thicker so that the energy transfer from donor to accepter so you just see what are that criteria’s.

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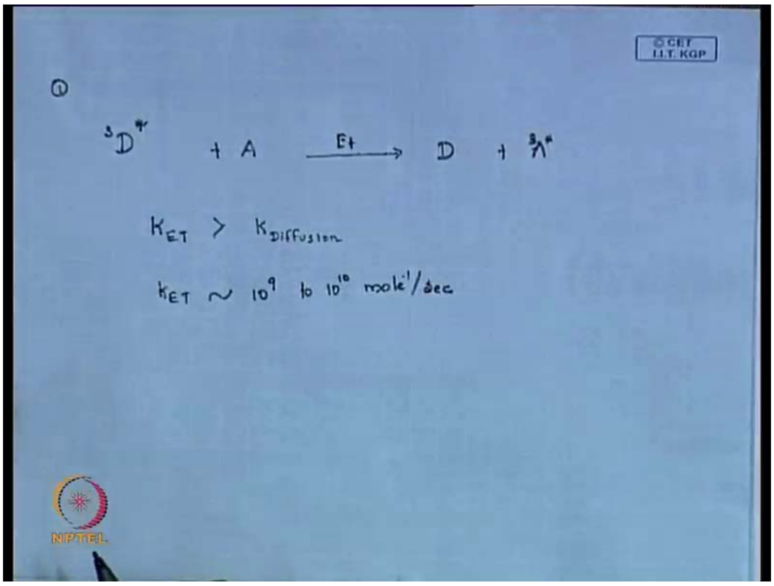

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$$^3D^* + A \xrightarrow{Et} D + {}^3A^*$$

$$K_{ET} > K_{Diffusion}$$

$$K_{ET} \sim 10^9 \text{ to } 10^{10} \text{ mole}^{-1}/\text{sec}$$

I will just deal with my first criteria that is what I said is that, have my donor which is in my exciter state correct, then I have my acceptor, so this 2 molecules has to come together they have to come here together then they have to colloid. What you think another process can happen when they are 2 nearby 1 is that they can colloid another before collusion can anything happen if 2 molecule comes near together. So 1 they can come closer and colloid another most of the time what is a competitive reaction happens in any bi molecular reaction they can easily diffuse they like to they can colloid or they can diffuse. Cleat because that is the process which happens in bimolecular reaction when 2 radicals or anything comes together they always have a competition reactions are diffusing away from each other right so instead of collusion they can also diffuse. So if the rate of diffusion is greater than your rate of collusion then there is no energy transfer. If the rate constant of your energy transfer rate of the energy transfer is greater than your diffusion.

Then you will be seeing your energy transfer reaction. That is a first most criteria so if they can colloid, then you can see the energy transfer. So what is the first foremost we can say if the rate constant if I say k e t should be all the time greater than your k diffusion. This should be your first criteria to be otherwise they will just diffuse way from each other they will not colloid they will not colloid and they will be no energy transfer reaction. Any idea what is the right constant of your diffusion? Normally any reaction if you do what is the rate constant for diffusion how fast it is? Because most of the reaction has been controlled by diffusion because molecule try to diffuse from each other so the energy transfer is 10 to the power of 9 to 10 to the power of 10 moles per second inverse k t most of the time. If you want the numbers and they are approximately 10 to the power of 9 10 to the power of 10 mole inverse per seconds so, your diffusion should be what number diffusion you think. Those studies 10 to the power of minus fourteen moles per mole inverse per second we have studied lot know.

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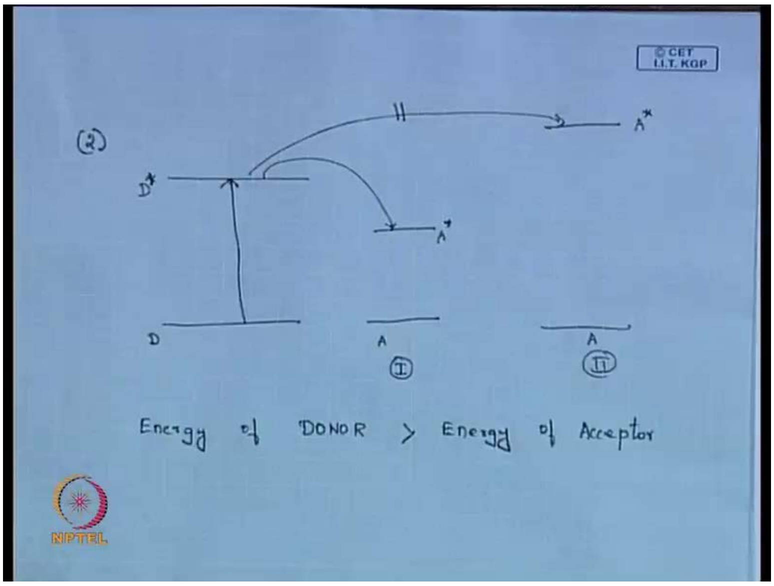

So most of the reaction what happens most of the time it tries to diffuse very fast because it’s very dominating process. If you overcome that process then seeing reactions and everything happen so, if my energy transfer is faster than diffusion then there will be proper energy transfer reaction happen that is your first criteria. Now we will see the second 1 another important thing is have a donor energy and how this is the excited energy of my donor. There are 2 options accepted can be 1 my acceptor can be energy like this a star or my energy of my acceptor can be like this also. I have 1 acceptor molecule; I have a second acceptor molecule. So this will be good to transfer the energy. I am going d to d start he first case will be good because it will be a Daniel process. It can happen this will be a type of an appeal which you do not want from dynamic a, so what it says it says that energy of my donor should be greater than the energy of my acceptor. right so this are the 2 important criteria’s basically for energy transfer reactions to happen 1 your energy transfer should be greater than your diffusion, second is that the energy of your donor should be greater than your energy of acceptor.

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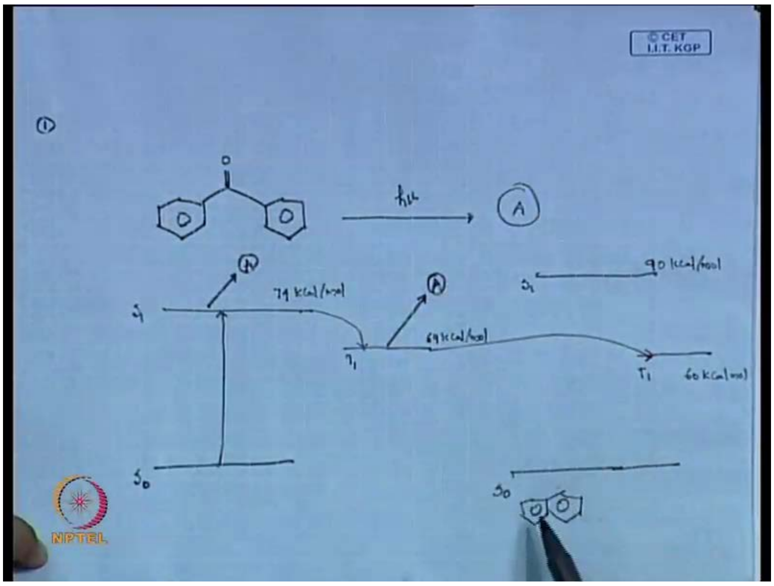

So these 2 conditions satisfied most of the time you can see energy is transferred from your donor molecule to acceptor molecule. Now what we will do so what is the great application of this, where we can use this chemistry for example, I am taking a benzophenone or you can take any ketone just for name sake I am taking is you will take any ketone if I photolysis is this I get a product I call it has also I take air take any ketone I get a product I call it as a or b whatever you can get any number of products. Then I am asking you a question whether this product A is actually coming from the singlet exciter state or it is coming from triplet exciter state or this product a is coming from both singlet and triplet. How to find it? like you have you are getting a product so people normally if you do photo chemistry the mechanistic point of view is that whether this happens from singlet exciter state or it happens from triplet exciter state or it happens either from singlet or triplet. If you have seen many things what we were can see reactions happening from both singlet as well as triplet. So, in that case how this energy transfer reactions will be useful.

So what I do is that I take this benzophenonei note the benzophenone energy values of benzophenone fine. So, what is s 1 energy value of benzophenone any idea you have studied that around exciter singlet energy of benzophenone 74 kilo calories per mole and your triplet is 69 kilo calories per mole so, what happens your s zero can go to s 1 from s 1 I can get the product at or it can undergo an inter system crossing to give me from triplet a bunt, right now I do not know from which side it is going on. So, what I do is that to the same system if I am taking twelve benzophenone and doing the photolysis to the benzophenone what I will do I will add naphthalene. So, you know energy of naphthalene you have studied that. So, this is around 1 ninety kilo calories per mole and sixty kilo calories for mole the t 1. What happens if you excite your benzophenone with naphthalene in the system so your s zero will go to s 1 then, it undergoes an intersystem crossing to t 1 then what it does from t one.

Because the t 1 of naphthalene is the lowest excited state. We see most of the time photochemistry happens from the lowest exciter state and from this it can transfer its energy to naphthalene, because that is what we studied from the triplet exciter state it can transfer then naphthalene then naphthalene will do the chemistry that I will teach you what naphthalene will do when we go for pi pi star chemistry. So, you will see pi pi star chemistry from naphthalene. Now our question was the product is from singlet or triplet if the product is from triplet for example, I am taking 1 assumption saying that the product is from triplet if I put naphthalene what will you expect.

If benzophenone is giving me a product a from the triplet exciters state for example, I am making an assumption, now I am putting a naphthalene in the system. So, what should happen to the product? the so that the product will not be formed so you cannot see the formation of a because your chemistry should happen from triplet but, now triplet what it does instead of forming a it will transfer all its energy to naphthalene. That means basically you are quenching your triplet exciter state. So, from that I can say yes my reaction is coming from my product a is forming from triplet exciters state. if my product is unaffected if it does not unaffected still I am getting the same product that means it is forming from my singlet exciters clear if half of the if I am getting like yield of hundred percentage but, I am getting only fifty percentage, then you can pretty well say that it is coming from both singlet as well as triplet so your quenching now triplet so still your getting some chemistry from singlet.

So that is why that is how you can know using this energy transfer chemistry. Whether from which state you can think about the product is forming, whether it is forming from triplet or it is forming from singlet or it is forming either from singlet or triplet clear any doubt. This we can basically we call as quenching process or you can call this as your quencher or donor acceptor or whatever concept but, this will help us to know this is 1 of the important application or energy transfer reaction. From state you are getting your photochemistry fine. Now we will go down and see the second application another important application of energy transfer reaction.

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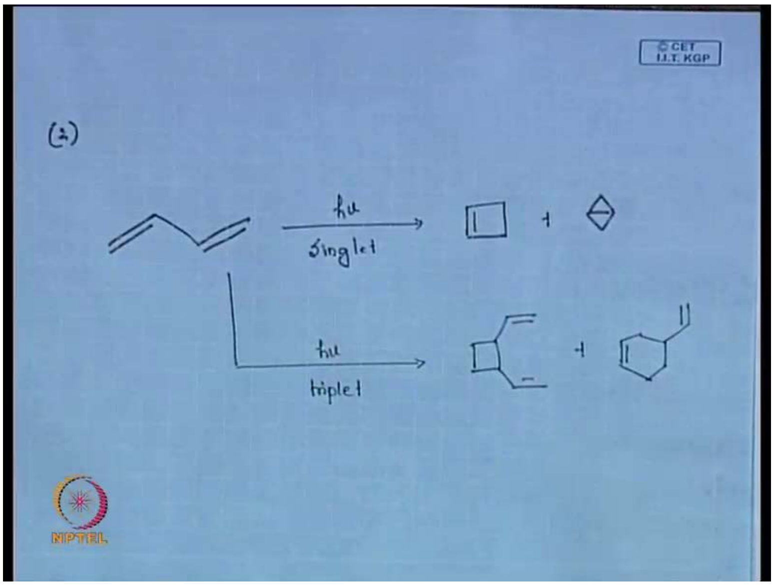

I take a type of beta there since we are going to study pi pi star chemistry next next next class so is better that you get into included involve introduce when I photolysis this see you know most of the timealkenesthe energy gap between your singlet and triplet is huge so you have most of the time you see chemistry happening from the singlet when you go from your alkenes pi pi star chemistry.

When I photolyze this I get 2 product I get a cyclisation this type o product. I will explain you the mechanism in detail how to form but, just we look for the application of energy transfer if it is done from triplet. So, I get this type of product your singlet is basically a type of cycloaddition of 1 unit of butadiene and you're in your triplet it is 2 butadiene is coming together and giving you this product. Now I say that see I want to make this molecule for any of my synthesis for I want to make this product and then I want to take use of this product for many making natural products or whatever. So, I say just I want take a butadiene photolysis I want only this product. I do not want this I want the chemistry to happen only from the triplet I do not want from singlet. So, what you can do you know that pretty well if I shine my butadiene if I shine light on butadiene it is going to go to singlet only and it is not going to do big intersystem crossing. So I will get only the products from singlet but, I do not want the product from singlet at all.

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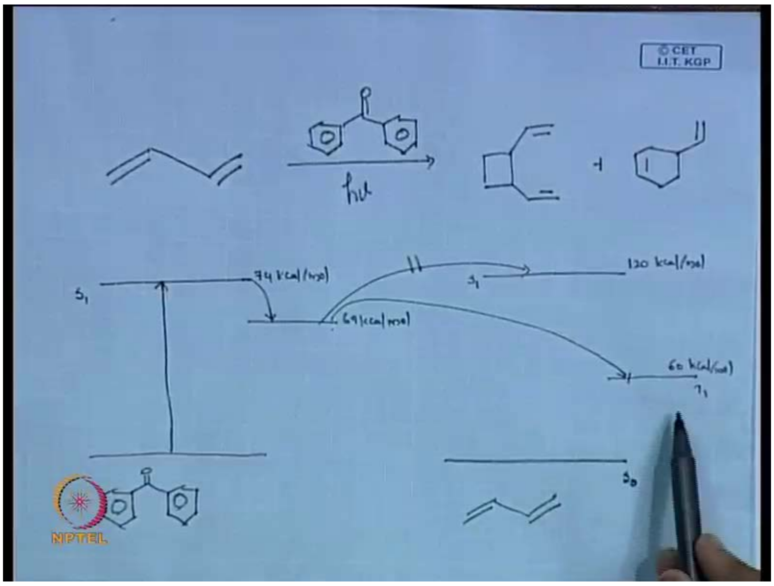

So what we can do in that case normally we use a type of sensitizer see for example, like an I take butadiene put benzophenone and do the photolysis. I do the chemistry like this then I get I get only this product show we get it so basically you know the energy of butadiene is s zero. This is 1 twenty kilo calories per mole this will be sixty kilo calories per mole sixty 1 twenty and sixty for butadiene singlet and triplet. Now I take what I will do I know my benzophenone energy. Sorry I just this is around seventy 4 kilo calories per mole sixty 9 kilo calories per mole. So, what I am going to do now is that I am not going to I have a butadiene as well as I have benzophenone and you know benzophenone observes light greater than 3 10 nanometer right 3 hundred nanometer and your dyeing system have absorption around 1 ninety to 2 10 so I can use a filter where the light can come greater than 3 10 nanometer and then I can shine only light on my benzophenone so what happens you know that it goes to s zero to s 1 then you know benzophenone undergoes very good intersystem crossing to give my triplet now this triplet can just transfer your energy to butadiene.

You know it cannot transfer the energy this way this is properly ruled outs it can transfer now the triplet state of your butadiene is got excited. So, I am not exciting now your singlet basically I am now your triplet has been excited now I get only the product from the triplet. I can bypass my singlet products so, this we call as triplet sensitizer benzophenone is normally triplet sensitizer this reaction we call a sensitizer reactions earlier we have seen a quenching type of reaction this reaction we call sensitizer reaction.

You can sensitize whatever straight you want because sensitize singlet or you can sensitize your triplet states and get that products from what state you want these are very feasible then you get only benzophenone you can remove a benzophenone out of the system. And then you get your products these are the 2 important applications of your energy transfer reactions.

So we have seen energy transfer reaction so we have seen that energy transfer reaction is nothing but, it is a physical process photo physical process where donor and acceptor comes and colloids and then the donor from the triplet transfer its energy to the acceptor. That is what we studied and we said that the diffusion your energy transfer should be greater than your diffusion the energy o a donor should be greater than your energy of your acceptor to take this. Then basically we study 2 important applications that you can use quenching study that means you can know from which state the products are forming then if you want you can excite that particular state and get your products. So, the that all about energy transfer reaction fine this we are going to use once you go to pi pi star chemistry most of the time you know pi pi star chemistry happens from singlet but, if you want triplet product then you have to use your source of benzophenone you should not take a sensitizer in such a way that it should do its chemistry instead of this I can take acetophenone and you know acetophenone undergoes alpha cleavage you should not take that type of sensitizer sensitizer is something which should just transfer its energy you should not do its own photochemistry. Then you will be getting the products from that.

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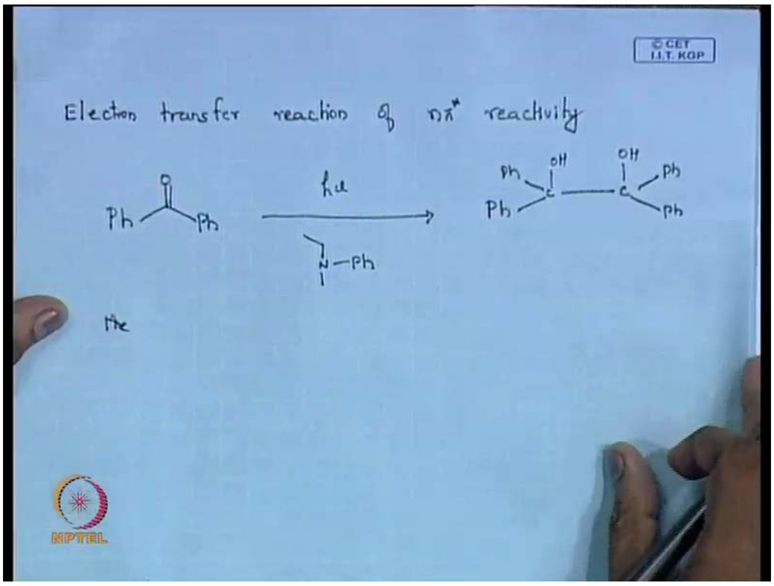

Electron transfer reaction of $n\pi^*$ reactivity

So the next reaction the last 1 of n pi star reactivity is your electron transfer reaction. We will see that now this is another class of reaction but, this reaction you have seen doing a photo reduction of benzophenone you have you have seen this reactions but, in this case instead of a any hydrogen abstraction from the solvent are used like the donors type of electron donors so I have my same way I can take my benzophenone. I take an (( )) photolyse in the presence of an for example, I take an (( )) like this I take your nice benzophenone called this we you have studied this reaction but, not in the presence of an amine but, you have studied in the process of isopropanol like different solvents you can get nice benzophenone but, in this case the reaction is little bit different so we will try to understand the mechanism do you know how far it is.

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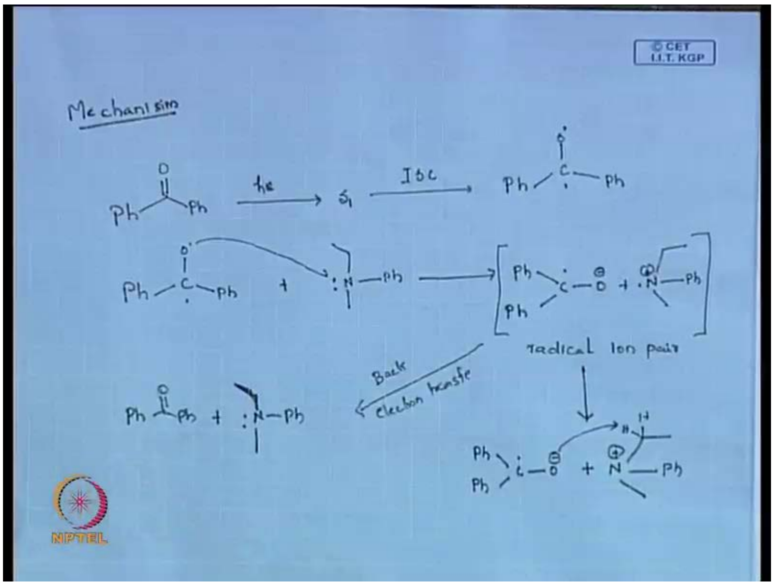

Cannot cover in 1 page so I will take the next page give the mechanism of this benzophenone you know that all this steps because now you are familiar with this. Now you have a step like this we have studied in the model of alkoxy radical what alkoxy radical can does in a model example we said that an alkoxy radical if it has an amine type of system it can abstract a non bonded electron from nitrogen then we call that reaction as redox type of reaction. We have studied we I just showed in the model component of an alkoxy radical in the earlier class so same way your o dot can abstract electron from a nitrogen atom to give me minus plus this would call as see you have seen many reactions were iron pair is formed were you can see but, this is a radical iron pair these are peculiar example were you can see radical iron pair we call them as radical iron pair and is most it is in a cages more like it is like a that is very important on this type of electron transfer chemistry.

Once your o dot fix off the nitrogen you get a radical iron pair and you get the radical iron pair using cage. See that is why I am saying the diffusion is very important if this 2 molecules do not diffuse for example, they stay like together then what happens then they can do back electron transfer. The electron can return back giving me the signing material, see that is very important in this reaction this is very computive process for your electron transfer whenever you do your forward electron transfer reactions you always get a back electron transfer that means these reaction is you can make it in the other way wrong that happens always that is the problem little bit problem with the electro transfer reaction you have to find put that in a system where there is no back electron transfer happens we call it as bet.

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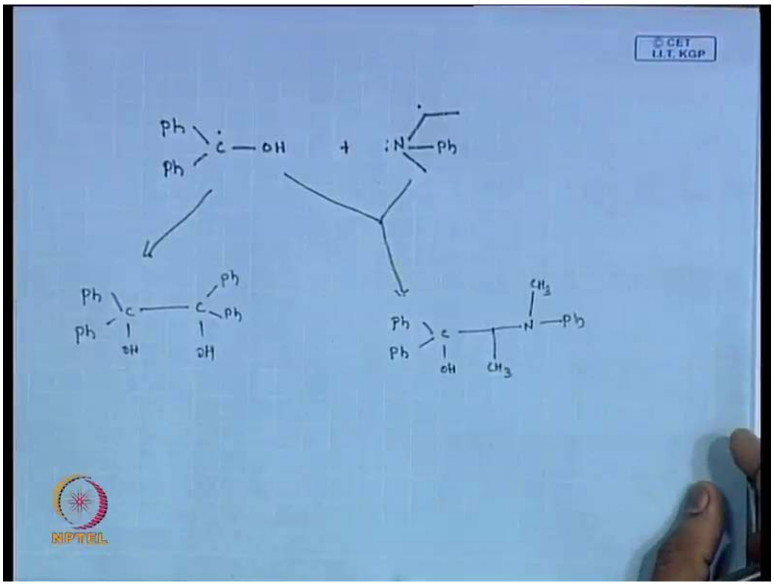

If it diffuse for example, instead of doing a back electron transfer you take a system in such a way that it tries to diffuse from the cage they come out very fast. Then you end up with the you get a system like this will be also in system now what happens this can o minus can abstract an hydrogen a proton transfer can always happen from here my o minus can go and abstract this hydrogen because this is the special hydrogen no top. That happens then I will end up with the system p h oh plus I can just shift this electrons to get me a system like this fine because I will get 2 electrons I will give 1 electron to the nitrogen make it n double dot with previous nitrogen electron and keep 1 dot here. So, then you know that this can combine with itself to give me benzophenone were you can expect or this 2 can combine with each other. We can see this type of products also you can get this type of products also, here it can make a bond that also (( )) but, this is the major product you get most of the time benzophenone so in electron transfer reaction you most of the time you should take care that you avoid this computive back electron transfer because that will happen most of the time because they form like a cage radical iron pair before diffusing they try to again do the electron back and then get to the starting material. So you but, since you know diffusion is very fast you get things happening to give you a products fine.

Now we will see what if there is any now this is itself says that you can reduce now your benzophenone which systems are you can form your c c bond formation all these things. We will see 1 good application recently has been done you see this electron transfer reactions you see that. See 1 good application you have studied about protecting groups right so you can take any acids you can protect your acid and then you use most of the time acid and base to be protected right so I want a system in which I do not want to use acid or basei want to be protected for example, I am taking an a I am taking an amino acid I am just saying for a example I take an amino acid I want to release the amino acid in the cell were I do not want to do any amine like a acid or base wash so I want to release just like that.

So what that case you can use your light so there are many protecting groups in which we can take an amino acid. You can attach to the protecting group by simple chemistry then you take to the cell in vitro or in y o and then you shone light now others you have very good system were you can use even visible light just shine visible light or you will light then slowly your amino acid will be released, because that is Avery good chemistry which is coming out right now in photo chemistry protection and deportation and people are using it for lot for biological purposes and if your if your protecting group basically is florescent then you can even image the cells like (( )) fine.

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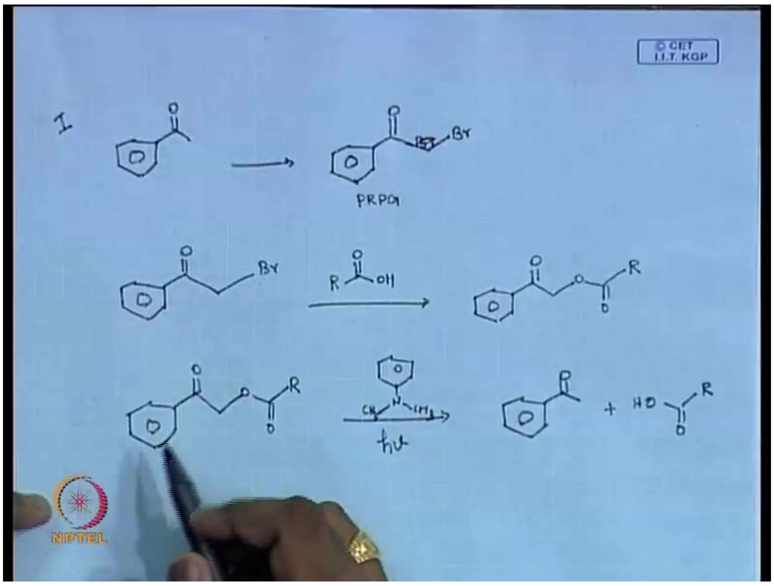

So I will tell you 1 example in electron transfer reaction how we can do that. For example, take your acetophenone yeah you know you can do your bromination alpha bromination you can note this. This will be my protecting group just it is a simple as per (( )) you take a bromination and b s or whatever bond you get your alpha bond so this will be my I call them as photo removal protecting group or you can call them as protecting group. This is c h 2 b so you get a c h 2 b r.

Now what I do is that I take this I can take with any carboxylic acid I want most of the time we use amino acids but, you can use any carboxylic acid you want. You get a nice protection right I can protect now this is simple protection see bromoacetophenone is available even we does not need to make it you take a bromacetophenone take an acid just stir it in d m with simple bases you will get your protection that is grows like a ninety 8 percentage then you take this now you say sir I want to de protect it so simple you take your compound protected compound use amines for example, I am using you can use any like if you want an amine which can observe an 4 10 nanometer which is greater than the visible like 4 10 in the visible region. You can make a amines like that you can get any amine you want depending up on your wave length and then just shine your amine you can end up with the (( )).

So we just see the how the mechanism works that is will be interesting so but, just you can photolyse this you end up with this product simple reactions now a days for cell imaging and releasing a fluorescent compounds are this are this are chemistries have been used. If you want to study some photo physiological reactions happening inside the cell you want to know how they how this cell behaves then you just inject your sample instead of this phenyl if I take pyrine then what happens this whole system will be fluorescent. You know your amino acids are not fluorescent so you do not know which cell it is going to bind but, if you hook a pyrine then you know it is fluorescent then you can just by fluorescent imaging you can know which cell it is going to bind. You can just watch them and once it binds then you shine your light so that the amino acid is released this type of works have been you can see many papers coming jacks like that. So, we just now see the mechanism how it works. See in this case what we can do see if you want you can excite your ketone but, in this case you can simply excite your amine also both are same.

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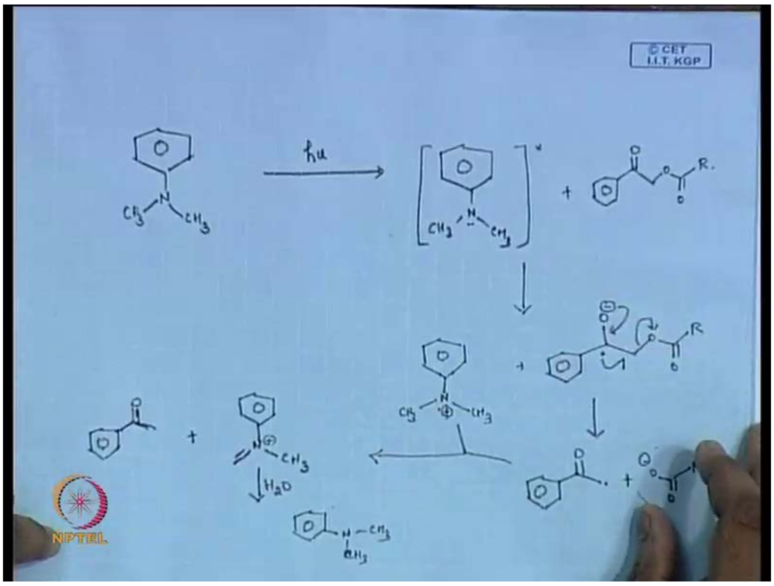

You can excite your amine here you can most of the time you excite your amine; amine gets excited system like this. Now your carbonyl can abstract an electron from your nitrogen. So, you can get a system like this. Fine so in the previous case we was we were seeing this o minus grabbing an hydrogen from your methane right that is what we saw in previous examples and you then can then you can make your radical perite. This time you can even you can think about this down. If I push this I can just move this radical it is a radical. The second equation is radical then I can push this up.

So if that is get no minus yeah that will be abstracting an hydrogen from the solvent tor from the system to give me a the amino acid back and then this 2 can this radical can abstract an hydrogen from your methyl to give you type of acetophenone here you get your acetophenone back plus we get your (( )) right if you’re doing this reaction in water then you do it then you think your amine get hydrolyzed. See most of this photolysis we do it in water because we want to do it with the system right and biological system .

I just abstract a hydrogen from here it is a dot radical. So, then you can hydrolyze this in water to give you normally you know that we get something systems like n h c s see that you can I get it in your hydrolyze so this is how the mechanism happens but, we are much more worried about your acids and you can see the acid is been released with you can release it in a high chemically it as well as you can release with a good contam efficiency now a days the recently what happen is that see instead of taking your amine need any electron donor that is all my idea is right anything which can donate an electron you think any other thing other than your organic molecules.

Which is now there are several paper’s in nature recent (( )). Whenever department also we are doing some faculties are doing so it contains gold nano particles. You can take titanium nanoparticals so you can excite them and you can take an electron from the bolt or you can take an electron from the titanic. So, what happens the carbonyl goes abstracts an electron from the titanium then the whole chemistry happens like this so just and you know the titanium observers in the region of what 4 10 4 forty 4 fifty so you’re going much more divisible so you can do this while chemistry in laser light. So if I want to release something in this cage so just I will take my laser light I can just show it for thirty micro seconds or 10 micro seconds my titanium gets excited my carbonyl takes the electron and releases my amino acids.

So my amine you can say amine is toxic but, I can think about nanoparticals which are not toxics like titanium gold nanoparticals many nanoparticles which are not toxic so you just have to add to them and just do it. And now a day’s people are doing even inorganic complexes like ruthenium. Ruthenium are well known to observe light greater than 5 hundred nanometers ruthenium complex so you make a ruthenium complex and you know ruthenium are very good for giving an electron. So, this guys goes and take an electron and do the chemistry see not only in this area see if I want to do a paternobuchi reaction for a example or any alpha cleavage or paterno alpha cleavage reaction we say that I want to do Norrish type 1 reaction or Norrish type to gamma hydrogen abstraction normally what wave length it goes.

We do in ketone so it is 3 10 nanometer so you need a photo operators for that so basically you will say sir the main drawback of photochemistry what you say sir I cannot do in synthetic lab because I have to get that photo lamps. If you overcome this you can easily overcome because you know that carbonyl can abstract an electron so put some titanium? instead of keeping that in the photo lamp keep it in your c f l bulb there are many chemistry as in publishing a it is a lot you all can get people do just by c f l bulb take your c f l bulb which is available just keep your r b flask and shine even it does not need a cover board, because it is just your bulb just you can rap with the paper and irradiate for half an hour you do all your chemistries your Norrish type your Norrish type to pattern up which 2 plus 2 addition all are now coming just by using your c f l bulb they are saying me to do anything buy the lamp we do not need any photo lamp do not need now photo lamps. That is how the pet chemistry has the electron transfer chemistry has improved, because I have a donor which can observe light in the visible region and then can donate an electron.

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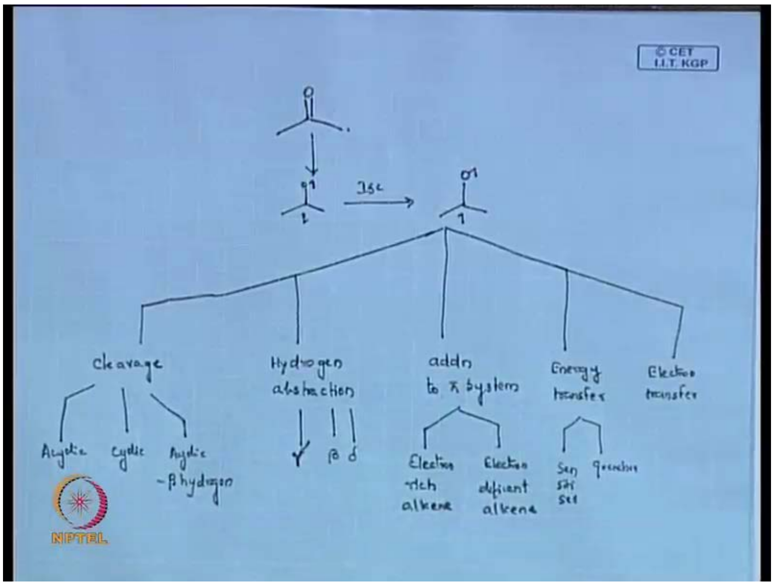

So that is nice know. So, that is what all about your electron transfer reactions you do not what yeah that can also everyone can diethyl. You want n or c h 3 you want that sorry oh your carbon has gone. Fine that should not be there so that is good so that is what we were just trying to understand about your photochemistry of n pi star reactivity. So, we have seen so as to conclude photochemistry of n pi star reactivity I will just generalize you some reaction just for short summary for 2 or 3 minutes. You just summarize just you summarize you have a carbonyl and you have heard this carbonyl can goes to singlet and then undergoes nice intersystem crossing that is we seen in carbonyl chemistry into system crossing is (( )) to give me a triplet. Right and we have studied based on this first reaction we was studied was cleavage reactions.

Then we studied hydrogen abstraction then we studied addition to pi system. We went to energy transfer and then we went to electron transfer. So, we are study this 5 set of reactions right so cleavage reactions we were thinking about what we studied in cleavage remember. So, we studied a cyclic right cyclic systems and then a cyclic systems having beta hydrogen right so we studied this 3 basic system in that. In cyclic as we studied 4 members 5 remembered and 6 member like that but, this are the 3 main groups we studied 1 is acyclic carbonyl system another is cyclic then we studied acyclic which has beta hydrogen. In hydrogen abstraction.

We delta mainly with gamma but, we said that apart from gamma hydrogen abstraction we say that we can also see beta right and we can think of delta and so on. The number keep on increasing so we say that even it is very further it can do an hydrogen abstraction addition to pi system we divided basically 2 we say that it should be electron rich alkene and we need for electron diffusion system also, in the last class we were discussing about energy in this class we were discussing about energy transfer and electron energy transfer I have shown you how the sensitizer works and your quencher. You studied both the things how you can sensitizer reaction how you quench a type of reactions, and then we studied about electron transfer reaction so these are the basically n pi pi star reactivity we (( )) so from next. So, that is all about n pi star reactivity next class that is we start with pi star chemistry photochemistry of pi pi star system. So, we end up the class now.