Organic Photochemistry and Pericyclic Reactions
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Lecture No. # 02
Introduction to Organic Photochemistry (Contd.)

So, in previous class we will be, we are gained something about the introduction of organic photochemistry. What will do in this class, we will also deal something more about the introduction part, because we left up to R to R star right.

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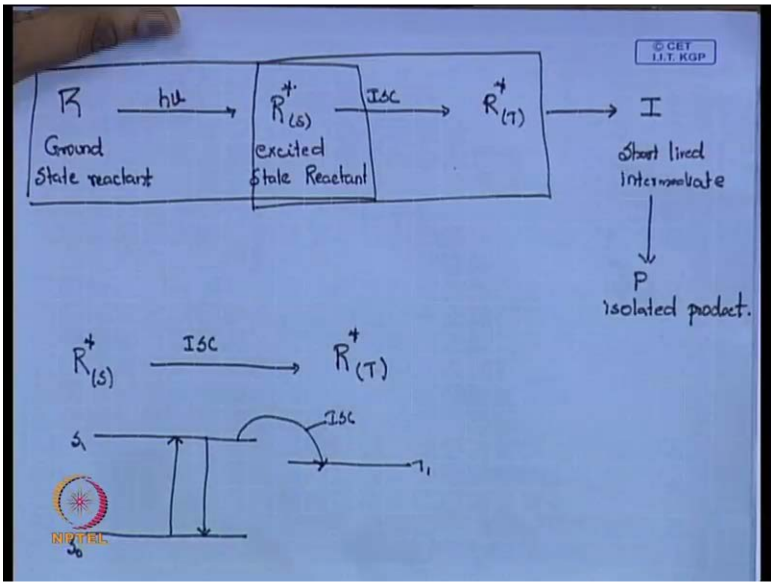

If you see now previous class, we discussed that you have an R, which is your ground state reactant gets interaction with your light which is your reagent gets excited, we call this as an excited state reactant. We said that it can go to your singlet state, then it undergoes an intersystem crossing to give you a triplet, which then gives you an I, you said it is a short lived intermediate, which gives you the P, which is your isolated product. So this was, we studied in detail or we just brushed up like, how your R can be converted to your P. Then, we went inside and studied in detail, how R is getting transformed into R star. So, that was what we discuss in the previous class.

Now, what we will do is that we will just put little bit inside into how this R star gets into R star triplet. So like, we will try to understand the energy levels of the singlet, and the energy levels of the triplet, what is going to govern, why this molecule as go from singlet to triplet, this energy level of this singlet and triplet have any meaning on that. That part we will do today, like we will just start with that fine.

So, we will be concentrating now on, how R star singlet is undergoing an intersystem crossing to R star triplet. So, we said that you have an S 0, you will be having an S 1, and you will be having a T 1. So, your S 0 can go to S 1. Now, this S 1 can come back to your S 0. It has an option of doing two things. It can come from S 1 to S 0, or it can do an intersystem crossing to your T 1. Now, it has a option of doing two.

Basically, the intersystem crossing, if you see it depends upon the energy gap of your singlet and triplet so is one of the factor. If the energy gap between your singlet and triplet is very small, then what happens? The molecule try to undergo an intersystem crossing rather than doing your photo physical. There are many other criteria’s like life time of your singlet and triplet, but now we will concentrate only on the energy gap. Your energy gap is small, this molecule try to do an intersystem system crossing, rather than doing the photo physical things.

For example, we will take an n pi star. So, I have my S 0, have my S 1, have a T 1. This is for my n pi star I am drawing. This is n pi star transition. So, I have a S 0, S 1, T 1.

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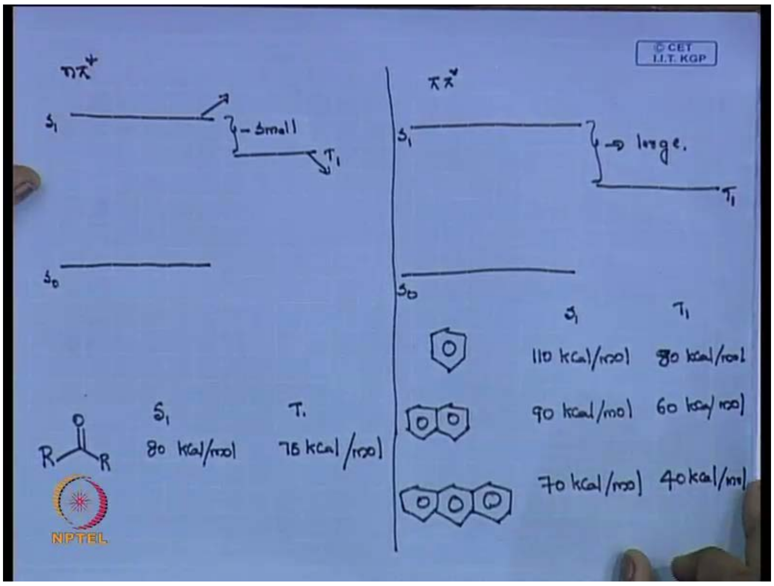

On the other hand, what I am going to do? I am going to draw for my pi pi star. So, I have an S 0, then I have my S 1 and I have a T 1.

Now, if you see or if you notice that, I have drawn that energy gap between singlet and triplet to be little bit smaller. When you compared to the energy gap between singlet to triplet in pi pi star. In n pi star the energy gap is small, when you compared to the energy gap of your pi pi star. This is little bit small and large.

So, now what will see is that small large, what it means, we see by numbers, then we can understand how small, how large it is. For example, I will take a ketone. If you see the singlet energy level of ketone, it is most of the time it is 80 kilocalories per mole, this energy singlet one, this is 80 kilocalories per mole. And if you see for your triplet, that is 75 kilocalories per mole. So, you have an energy gap of only 5 kilocalories per mole.

Same way if I go for my pi pi star, and see what happens? What is the big number there? I draw for y benzene. Any idea, what will be the energy level of the singlet for benzene? Anyone?

So, it 110 kilocalories per mole, if I go for my triplet, it is 90 kilocalories per mole. So this can be 90 to 80 depends upon this one yeah, if it is 80 kilo calories per mole. So, you have an energy gap now of 30.

Same way, if I draw for naphthalene, it has of energy of 90 kilo calories per mole singlet and your triplet is 60 kilo calories per mole, if I draw for anthracene, it is 70 kilo calories per mole and for this it is 40 kilo calories per mole. So, you see the energy gap now. For n pi star transition the energy gap is only 5 kilo calories per mole, but if you go for a pi pi star transition, it hangs around about 30 kilo calories per mole.

So what I can say from here, when I do n pi star photochemistry. My photochemistry will be most of the time dominated by my triplet right. I can see my photochemistry happening most of the time from the triplet state, because all the molecule gets excited to singlet, then since the energy gap is very small, they all undergoes a intersystem crossing to give me triplet. So, I see all my photochemistry happening from the triplet, but when I come to my pi pi star, so what I can see? Any idea? I can observe photochemistry both from singlet as well as triplet. So, pi pi star chemistry most of the time you can see photochemistry happening from the pi like singlet state as well as my triplet state.

So molecule, some other molecule tries to do intersystem crossing, and then do the chemistry from the triplet, some of the molecule says I am happy in the singlet, because I cannot jump 30 kilo calories, so I can do my chemistry from singlet state. That is why, this energy gap matters a lot in deciding the photochemistry, from which state it does clear.

Now, what will do is that? Now the next question comes in the mind. Why n pi star energy gap is small? And why pi pi star energy gap is huge? We will talk about. Why the energy gap between n pi star is only 5 kilo calories per mole, but when you go for a pi pi star it is 30 kilo calories per mole.

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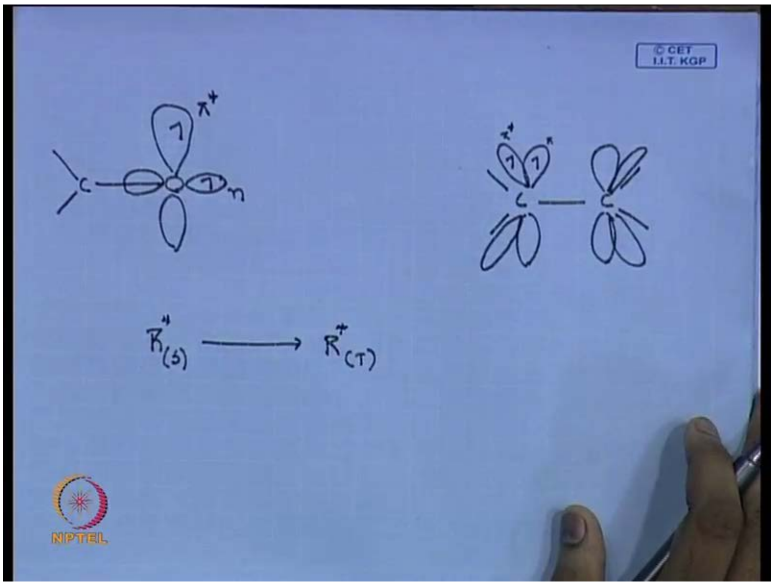

So, for that what we will do? Just we can understand based on your orbital picture. See, if I write about taking for, write for first. See, I am trying to draw triplet of pi pi star. So, I have an electron here, I will have my electron like this. This will be my pi, and this my pi star. So, what happens? You will get a very good repulsion. So, repulsion between your pi to pi star will be large, when I draw for my n pi star, if you just watch our, if you draw for my n pi star.

See, now you can see the repulsion in n pi star. So, your repulsion in n pi star should be in this case very less. When you go for pi pi star, it will be high. That is the reason, why your n pi star energy gap is only 5 kilo calories per mole, but when you go for a pi pi star, the energy gap becomes more, this is the reason. Just by orbital you can by repulsion clear.

So, we can say that now, we have atleast some idea. How this R star singlet is getting to R star triplet, and how they dominate over your photochemistry, whether the chemistry has to take place from to triplet, or the chemistry has to take place from singlet, or either singlet or triplet. this all depends upon the energy level of your singlet and triplet.

There is another future which will slowly consider, will be your life time. Life time of your singlet and life time of your triplet that also will come into the picture, but right now we will think about the energy level. That is the first criteria. So, that is good.

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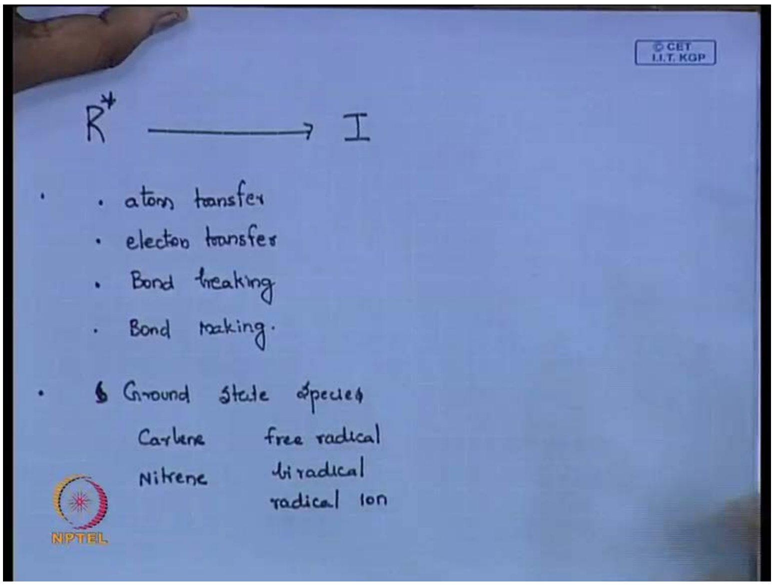

$R^* \longrightarrow I$

- atom transfer
- electron transfer
- Bond breaking
- Bond making.

- Ground state species

Carbene free radical

Nitrene biradical

radical ion

So, now we know how to move from R to R star in detail. Now, slowly let we understand, how we are going from my R star to your nest I, that is your nested, how this R star is going to get into I.

As I said that, once a molecule gets excited to a excited state reactant, that is your R star, it can undergoes some major sort of chemical reactions like your R star can do an atom transfer, it can do an electron transfer or it tries to do your bond breaking, it can break a bond, or bond making, or you can bond formation or bond making, whatever it is. So, this four things can occur from your R star. Your R star can do either an atom transfer or it can do an electron transfer, you can break a bond or it tries to make a bond to give you a intermediate I.

So, what is this intermediate actually, the first thing you have to remember, most of the time you go wrong is that, see the intermediate formed is again a ground state species. The intermediate is not an excited state, it is a ground state species .

You know that a ground state species, most of the time is singlet right, that you know, except your oxygen, most of the time your ground state species are singlet, remember that. So, it forms a ground state. So, now the question you ask is that, why we are not able to isolate this. This ground state species is so reactive, like, it does an intramolecular hydrogen obstruction within itself, or it can do and intramolecular hydrogen obstruction from outside inter or intra.

So, the reactivity of this, I is so fast. So, it forms me the stable product P. That is why, we are not able to isolate this I, but it does not mean that this intermediate is in the excited state. This intermediate is a ground state intermediate. So, the best example for that is, your carbene, it can have your nitrene, you can get free radical, biradical, radical ion like carbo cations, carbonium all those things will get into your intermediate species. So, this is your I.

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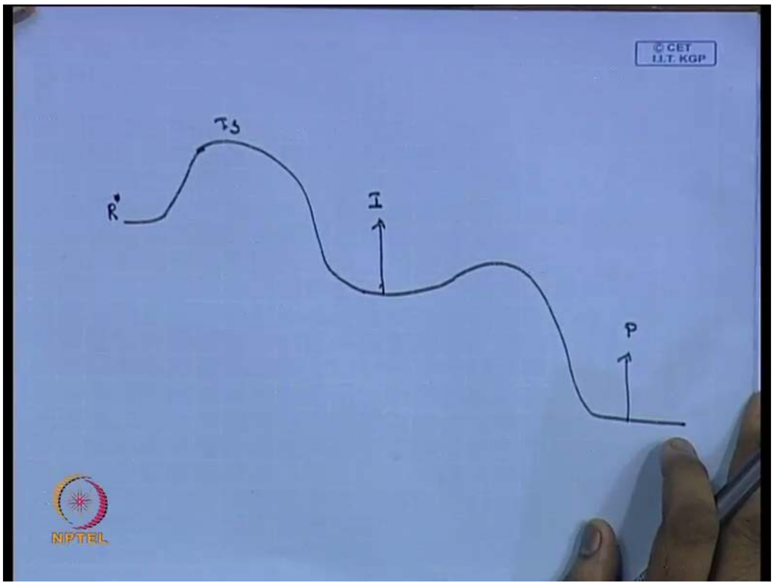

Listen, so same way if you see the energy profile, how it looks like. See, I have my R star, it goes to a transition state and gives me I and it goes then it gives me a T. So, this will be my transition state, this will be my intermediate I am talking about, this will be my product right. So, where your intermediate stop this idea. So, it says that, my product is still in lower energy. That is why, this is to the isolated product, not this guy. That is why, I am saying. So, this will tell you this energy profile that, it is not the really stable product, which you can isolate.

The important thing now to remember in this intermediate is that, the spin of your intermediate most of the time will be exactly same of the, your excited state reactant.

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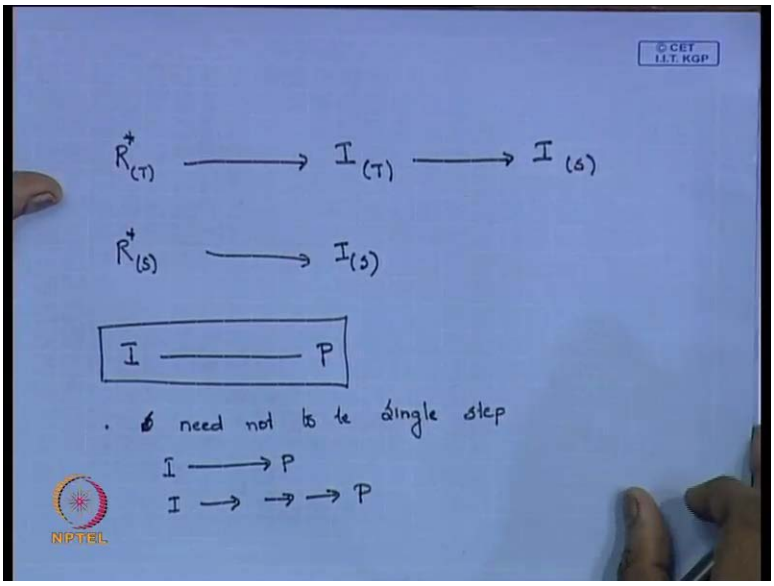

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$R^{*}_{(T)} \longrightarrow I_{(T)} \longrightarrow I_{(S)}$

$R^{*}_{(S)} \longrightarrow I_{(S)}$

$\boxed{I \text{ ——— } P}$

- need not to be single step

$I \longrightarrow P$

$I \rightarrow \quad \rightarrow \rightarrow P$

NPTEL

What I am saying is that? See I have an I have R star, which is from the triplet and you know your intermediate is what? Is a ground state species and it should be singlet, but it does not happen like that. What it does? First, it forms you an intermediate of triplet, then your triplet intermediate, then changes itself to singlet. That is why, I am saying the spin is most of the time is same as that of your excited state reactant, this very important thing. Because your intermediate spin, most of the time will be the spin of your excited state reactant. It does not have much time flip around, to give a ground state species.

So, your reactant excited state reactant breaks and gives you the intermediate. It does not have a time to flip around the electrons to give you the ground state. The ground state intermediate then turns, changes its spin to give you a ground state singlet its clear.

So far, if you are getting from an R star from the singlet, I said in pi pi star chemistry, you can see photochemistry from the singlet also. In that case, you can directly get your intermediate of singlet. That is why, I said that intermediate, the spin of your intermediate, most of the time are same of the spin of your excited state reactant clear. So, this are the points which you have to remember when you move from R to I.

First I say that your R star, can do some sort of reaction which will be your atom electron transfer, then your bond breaking bond making to form your I, then I said your I is a ground state species, but it is very short lived, due to his reactivity. And then, I said that is the spin of your ground state, spin of your intermediate will be most of your time exactly same to the spin of your excited state reactant clear. This is how you change from your R star to I.

Now, what we will do, this the final one, which is this most of the time the simple one, it is your I to P which you are studied, because you know, because this is mostly a ground state reactivity which you are studied I to P. The two points you have to remember when you transform from I to P is that, one the I to P can be a single step or it necessarily need not to be a single step, it can be multiple steps. That is the first point you have to remember, it does not need not to be single step. So, your I can transform to P like this, or your I can do a multi step process to give you the P.

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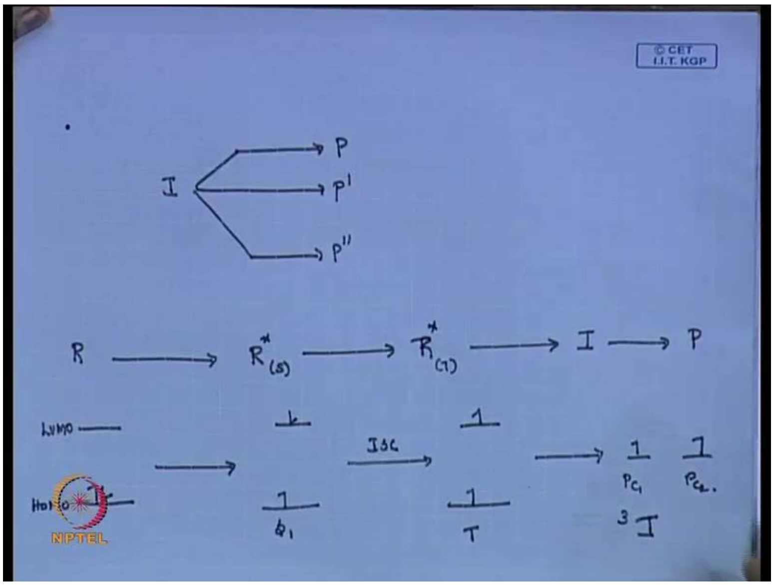

The second point you have to remember when you talk about I to P is that, this is most of the time happens in the photochemistry. That your I will not give you is not necessarily that you have I has to give you only one P, that is one product. I can give you different products. So, you can get two more than one products when you transform from your I to

P; these are the two things you have remember when you talk from I to P, intermediate to product. It can be a single step or it can be a multi step, you can get not only one product, it can give you to several products right.

So, this what we look for, from R to totally to your P. Now, what we will do? We will take all this idea and summarize them together and say this is the big idea of the photochemistry. We can do, we can represent simply by words, then we will do some orbital, that is also simple that we do.

First, what we studied we have an R, gives you a R star singlet. R star singlet will give me a R stat triplet, it can give me intermediate and that will give me a product p.

If you write with respect your lumo and homo, just by electron spin, then I can write like this. For example, I am talking about, so what you get? First, you get your S 1. So your spin most of the time will not flip right. That is, what you studied in franck condon principle.

So, that will be your S 1. Then, it undergoes a sort of intersystem crossing, to give your triplet. For example, I consider this R star that is a triplet R star is trying to undergo a bond breaking process, bond breaking. You are breaking, a c c bond or whatever. Then I can write my intermediate like this, like I can say it is a P orbital of c 1 and P orbital of c 2.

So, by see the spin what I am maintaining? I am maintaining a triplet spin, because it is a, it comes from the triplet R star. So I am getting a triplet I. So, I can say my I is triplet.

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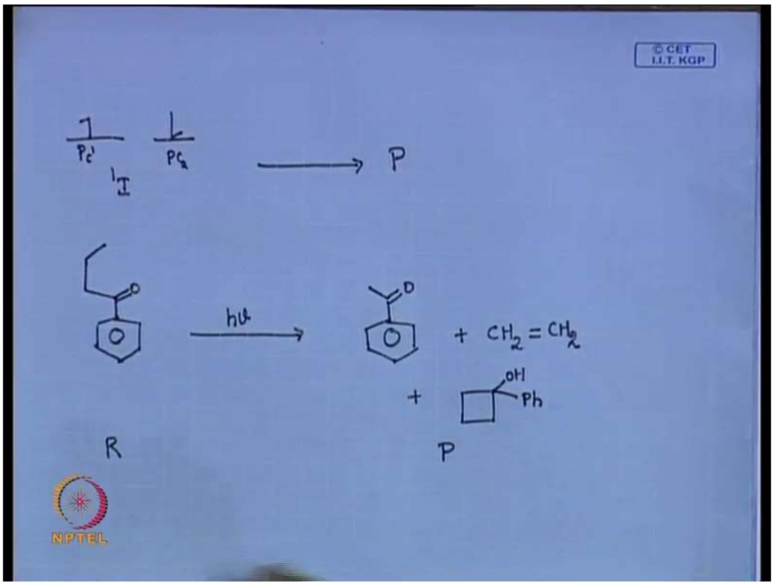

Now, what happens this triplet I, makes a spin flipping to give me a singlet I, to give me the, my final product P. So, this will call as a big idea of photochemistry. Any doubt up to this?

So, what we will do now? We will take a reaction, a organic reaction and see that, how we can represent that, by a simple representation of photochemistry and big idea of photochemistry, how we are representing?

For example, I am taking a ketone and photolysis part. Basically, I am doing it around 310 nanometer. So, what happens? Get this one product. So, this will be your simplest representation of your photochemistry, like what we said? You have an R star, you have an R, this is your ground state R and you have a ground state P. So, this is the first we started our class, we said that this will be your simplest representation of your photo chemistry. if I want to see in a big idea, how this R is converted, then we can write the same reactions like this.

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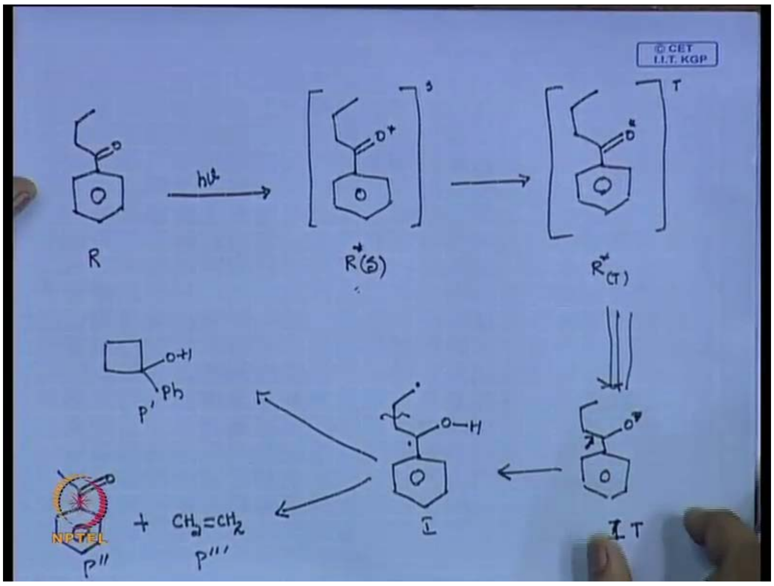

So, how I write? I say that h nu, this is my R. I am doing a sort of n pi star transition, because is, I am shining a light of 310 nanometer. So, my carbonyl gets excited. So, you can write this as a singlet R star.

First, it happens to be your singlet right, or you can put like this your singlet with an excited ketone, you can write like this also. If you want to put your spin, you can put also take the bond and you can put the spin. You can put a triplet here, R star triplet you can write like this. So, you know what happens? So, it forms then, so you get a intermediate I, so this should be a triplet intermediate yeah. So from here, I told you that, this I can give you different products. So, for example, you can make this much more legible like, I can get this stage, then it picks an hydrogen from here, you can make this as a I.

So, you can make this as your I, not this. This will be happening in your triplet state itself right. This you can call as a triplet spin, if I put the spin, then will be a triplet. So, you have your I now. So, what is this I? It is a nitrine or carbine or diradical, what it is? It is a 1 4 right, 1 2 3 4, it is a 1 4 diradical.

So, you know what 1 4 diradical does? It can cyclise give me this product, or what it does? Bond breaking, what bond breaks? Here breaks this bond I am right. Then it undergoes a type ketone or (( )) to give you, your ketone plus it gives you, your alkene.

So, now you have an I, this we call as one product, you can call them as prime p and (( )). See, this is my ground state product, which I can isolate. So, this is your simpler representation.

So, you have an R gets excited to a R star singlet, then it becomes a R star triplet, I have written in this way is not an equal, it should be like this. So, it is a spin, I have written a spin for a triplet and then, this can abstracts an hydrogen to give me an intermediate, which is a 1 4 radical, that can do ground state reactivity. One, it can cyclise or it can undergo a bondly wise to give me this product. So, that is how, we can represent a organic photochemistry.

This is the first one, which I showed is the basic representation, how you want to represent, you can represent just R and P, or you can this is a big idea of saying the organic photochemistry. So, one more thing you have to know, before we finish the introduction. That is, your yield, quantum yield, that part you should know.

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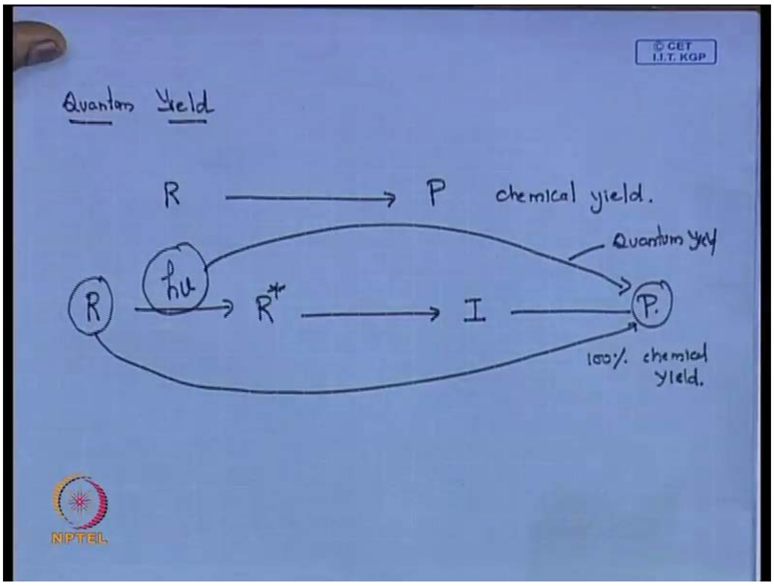

So, you know what is a chemical yield, basically right. Because, most of the time as an R chemistry know out, what is a chemical yield right. For example, you have an R it gives you P. So, how you know this reaction, how you say this reaction is 100 percentage, it gives all my R is converted to P, how you say that, this reaction is 100 percentage based on chemical yield. How you say?

No, I am not talking about quantum yield. Just an organic chemistry, by taking an substrate, you say that the reaction is 100 percentage, based on chemical yield. How you say? (()) no no with respect to chemical yield.

So, you take a one mole of your, if you take one mole of reactant. So, when you say the reaction is 100 percentage. So, you take one mole of your reactant and you should get one mole of your product, then you say the reaction is 100 percentage right.

That is, just a chemical yield for any reaction it is, but once we go to the photochemistry, you have an R. So, same way I can say, if I have an R, I take one mole of an R and I get my P completely. That is my R is converted to my P, then I say this reaction is 100 percentage right. So, I say it is 100 percentage based on the chemical yield.

So, your reaction can be a 100 percentage, but the important point here in organic photochemistry is that, most of the time we are not call a reaction, its efficiency based on chemical yield. Most of the time we talk the efficiency of an organic photochemistry based on its quantum yield that is based on the photons. See, if I have an h nu, that is my reagent right.

So, if I take whatever like, one mole of photon of what about. How much of product I am getting? Then it will be my quantum yield. See, when I talk with respect to my reactant, then it is chemical yield as your chemistry, general chemistry, but once I talk with respect to my photon, then the point of quantum it comes into the picture, this we call as quantum yield. So, you have to talk with respect to h nu.

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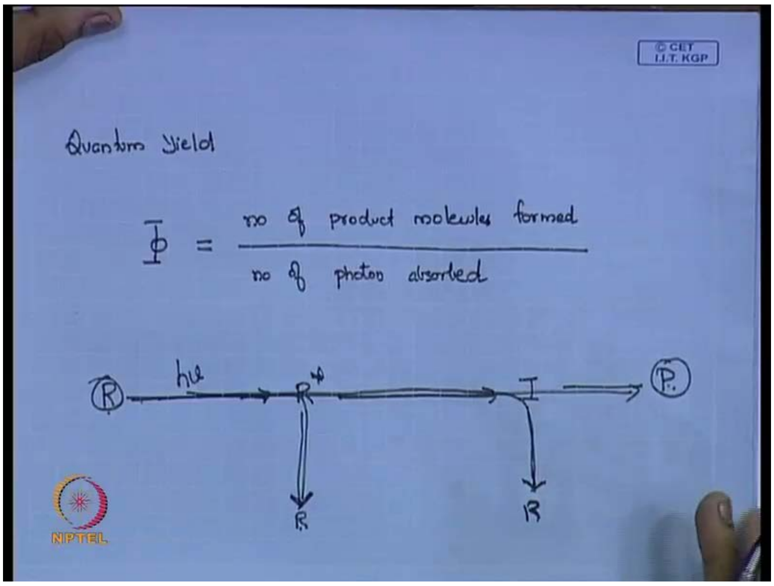

Quantum Yield

$$\Phi = \frac{\text{no of product molecules formed}}{\text{no of photon absorbed}}$$

Now, the question comes is, what is quantum yield?

Now, the question comes is, what is quantum yield? So, you use this symbol for quantum yield right. So you say, any one, what is quantum yield? So, number of product molecule form, see your quantum yield can most of the time we calculate the quantum yield based on your product.

You can also calculate the quantum yield with respective to a substrate also, but if I have like 2 3 products. So, it is better that I calculate with respective to my product right. So, number of product molecule formed divided by number of photon absorbed, so that you call as quantum yield. So, the question is why this is so important? Why we are, we can talk with respect of chemical yield and leave the chemistry right. Why you want to talk with respective your quantum yield?

See, I have now my R giving to me to R star and my I and my P. As I said that, if my R gets completely converted it is fine, that it is an 100 percentage chemical yield, but you see, if I take one photon, and this one photon transverse my R to R star, but what happens to this R star? This R star can give me my R back, there are chances right, this R star coming to give me the R.

So, what that, and same way, my I also can give me R back. So, what happens? If I use like three photons; for example, just for three photons, or you can say one photon. So, I am using some photon for this reaction, same amount of some photon I am using for this, and I am using. For example, I have one photon, I cannot correctly divide, just by numerical I am saying. I have a one photon, so I will be using 0.33 for this process right, so and another 0.3 for my I to R, and another 0.3 I will be using for R to P.

So, the reaction might be 100 percentage, my all R is converted to P that is fine, but if we talk with respect to photon what happens? It is only like the reaction has with the only your 0.33 photon has been used for converting your R to P, rest of them it has been inefficient right.

All you what happen? All you R star went to R and did photo physical property came back, or your I again reback and gave me the R. So what happens? I am use this photon of nothing, not for converting my R to P. So, we call these steps as inefficiency step.

R to R, R going to R star, then coming back to R, R going to I and coming back to R, R we call as inefficiency step.

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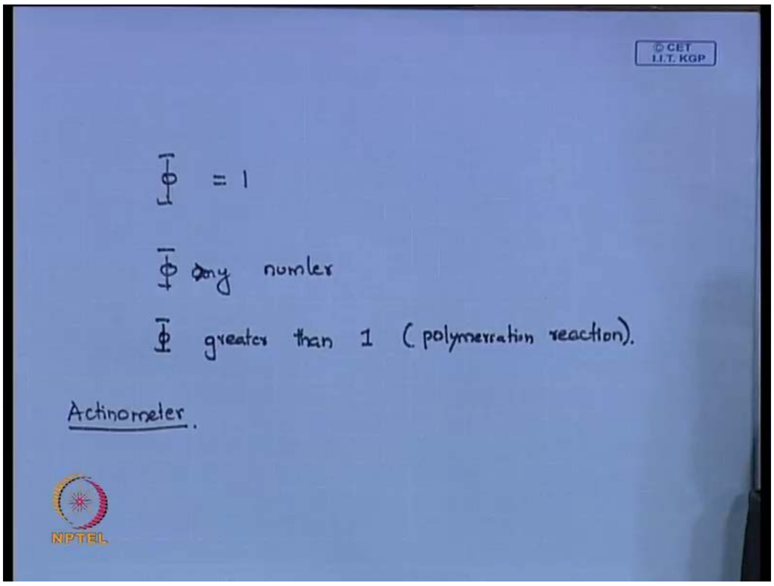

$\Phi = 1$

Φ any number

Φ greater than 1 (polymerration reaction).

Actinometer.

That is why, most of the photochemistry may getting your quantum yield one. Getting your quantum yield equal to 1 will be really hard, most of the photochemistry reaction. Because, you know that, all the time when the molecule goes from your R to excited state, it has a competition, it can do its photo physical or it can do a photochemistry.

So, you are not going to convert all your R to R star. So, people you can say that quantum yield can be any number, it can be any number, it can be a fraction of any numbers, but having a quantum yield of one, most of the time is R, more it is very hard process. There are process which have, but you do not see much.

Some cases, you see quantum yield greater than 1. In some process you see quantum yield greater than 1. What are that process? Yeah, you have polymerization type of reactions, where your quantum yield will be greater than 1 right. That is good.

How to, so your quantum yield will be any number, I can say it can be any number, quantum yield will greater than 1, you can observe can polymerization reactions or chain reactions.

Now, one more thing is that how to calculate this quantum yield, there is actinometers which we call, you can use a actinometers. There are actinometers available, or you can use actinometers like reaction based actinometers you can use. For example, you know velero phino chemistry.

So, what you do is that, you take a velero phino and do this chemistry, and you know for this much of light, how much velero phino you should get? So, you keep a velero phino, and on the side by you keep your reaction parallel, and then you can compare and from that, you can find out your quantum yield.

So, most of the time we use actinometer to calculate our quantum yield, but that part you will, I will explain you, when we go for the experimental session. That there are many instruments which we can use for actinometers, there are solutions which are available. That I will list it out, and it depends upon the wavelength. If you are using 410 nanometer, then you have to use different type of actinometers, when you use for 310. So, it depends upon the reactions, and there are solid instruments which can directly find out the light. So, that part that we will be discussing, but you should know quantum yield, you can calculate based on your actinometers right.

This one more part like, which we have to see is, there are some product inefficiency steps, like I said there is a inefficiency step of a R to R star. There are one more part which we call as product inefficiency step, that also we will be involved when we do some quantum yield calculations.

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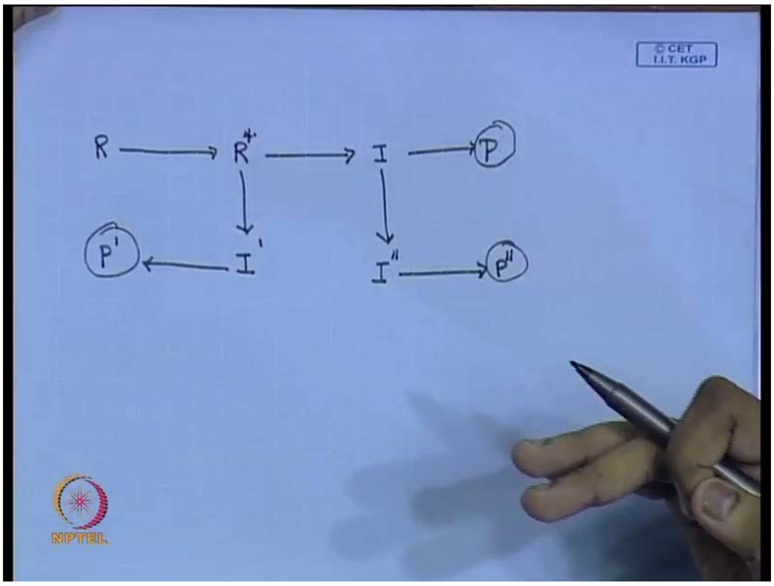

That is very simple, like you have an R, it can give you an R star, and this R star can give me I and then P right. See, it not that my R star is going to give me back my R, does not mean that has to give my R. Sometime what happens? your R star can also give me another intermediate I prime, that also happens in photochemistry reactions.

So this I, it does not need to give me back my R, this I can give me I double prime. So, I can from I prime, I can get my product. Another product which we call p prime and I double prime, we can get an another product we call as P. So, we call this as an another competive product inefficiency steps.

So see, if you want to do the quantum yield calculation, in this case what you'll do? If you want to do a quantum yield for your reactant. So, you are saying number of reactants divided by a number of photons, that time what happens, you go wrong, because you are getting different products now.

So, in this case, we will try to do the quantum yield, based on your product. I will say the quantum yield for the product P is 0.335 and the quantum yield for the product p double prime is different, and the quantum yield for the product.

So, here that is why, I said. It is number of product molecules divided by number of photons, if the reactions is a single step, that it gives R to P only one product. Then you can talk number of product molecules or number of reactant molecule disappeared, divided by number of photons, but there are very few cases where an organic photochemistry R gives you to P. Most of the time if you do an photochemistry reaction, you get like n number of products.

So, that is why, it is safe to calculate your quantum yield with respect to product molecule rather than reactant molecule clear. So, that is what the another point you have to remember in quantum yield.

So, your what I have said is that, an organic photochemistry you never you can calculate with respect to your chemical yield, but that is not so much better way to do it. So, we calculate with respect to your quantum yield, that is the first point you said.

Then, we said that quantum yield is nothing but it is a number of product molecule divided by number of photon absorbed. Then, we said one point again your quantum yield can be any number, it is very hard to find out number one, quantum yield equal to number one is very hard. There are many reactions where your quantum yield is greater than 1, that is a chain reaction polymerization reactions takes place. Then, we studied there is a inefficiency steps happens. That is why, you have to calculate with respect to your photon rather than talking about the chemical yield, then we said, there are number of you have to calculate with respect to product molecule rather than with respect to a reactant molecule right. So, that is how we did quantum yield.

So, I think the introduction of organic photochemistry you can finish your introduction with this, and then what we will do we will start, now the introduction part is over organic photochemistry. Now, we will start getting into the reaction slowly, like what are the reactions this, we will take organic molecules and try to understand their reactions. So, the introduction part, most of the introduction part is over with this.

Any doubt on the introduction part? Because, that is all its over introduction, I do not want to any point you guys want to ask likes like previous class what we did, how we move from R to R star, because you ask you are studying u v spectroscopic class also. So, you should know that how we any doubt there in the R to R star transition, because that part is very important, your R to R star when you shine a particular light, what type of transition I am going to look for, whether I am going to look for an n pi star transition, or a I am going to look for a pi pi star transition. Then, you talk about your singlet, and triplet there, any like the energy gaps, life time, after that you talk about your intermediates, and in your final photo products.

I want to know that, if you have any doubts, you can just clarify now itself, before we enter into the reactivity, because next I am going to take reactivity of n pi star chemistry, organic reactivity of n pi star chemistry. So, what we will do is that? Will, see we will start organic reaction of n pi star, and we see the all the reactions of the n pi star. What n pi star transition can do? What are the reactions, and then we slowly go to the pi pi star reactions, and see what are the reactions pi pi star can do your pericyclic reactions will get into this pi pi star scheme slowly; n phi star may you do not see any much reactions happening.

Any idea, what n pi star reactions takes place? What are the reactions n pi star can do…

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What type of reactions I am not molecules, n pi star chemistry. If I take a carbene, for example, I take a carbene molecule, shine a light of 310 nanometer. So, you know that it goes to singlet, then it undergoes an intersystem crossing to triplet. So after that, what are this reactions normally you see, what are the chemistry you can think, what my triplet n pi star can do?

Yes come on it has dimerisation little bit less pi pi star does dimerisation right .You can see any other good chemistries, any other good chemistry.

So, what I will do is that, I will leave with this, you can have a break and then we will have a next class, I will start about n pi star chemistry. We will see, what are the reactions this class I do.