Pericyclic Reactions and Organic Photochemistry
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Module No. #01
Lecture No. #01
Introduction – Activation of Chemical Reactions

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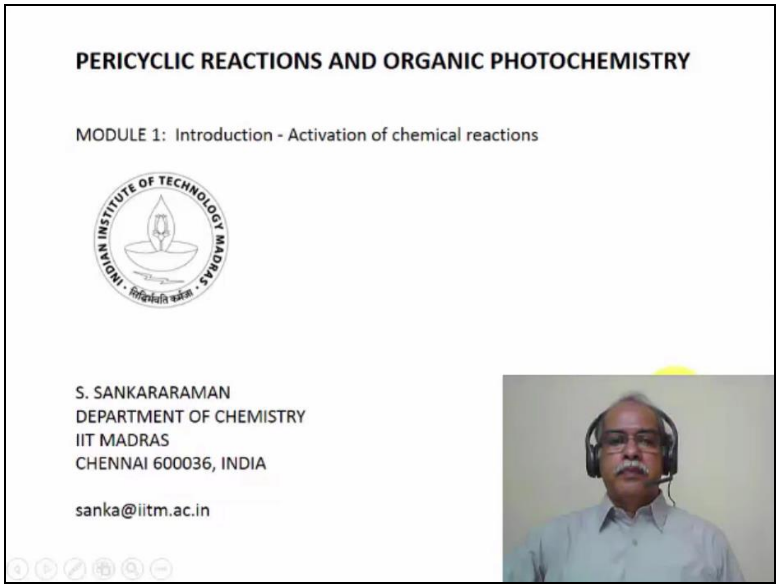

Hello, welcome to the online course of IIT Madras. I am Sankararaman, from the Department of Chemistry, IIT Madras. I am very happy to offer this online course on Pericyclic Reactions and Organic Photochemistry. Both these topics, pericyclic reaction and organic photochemistry, are offered in the postgraduate level chemistry programs, particularly in M.Sc chemistry programs.

So, if you are in the final year B.Sc chemistry, or M.Sc chemistry program, or if you are doing a PhD program in chemistry, you will find this course very useful. This is the first module of this particular course. And, i would like to introduce the concept of activation of chemical reactions, by couple of examples here.

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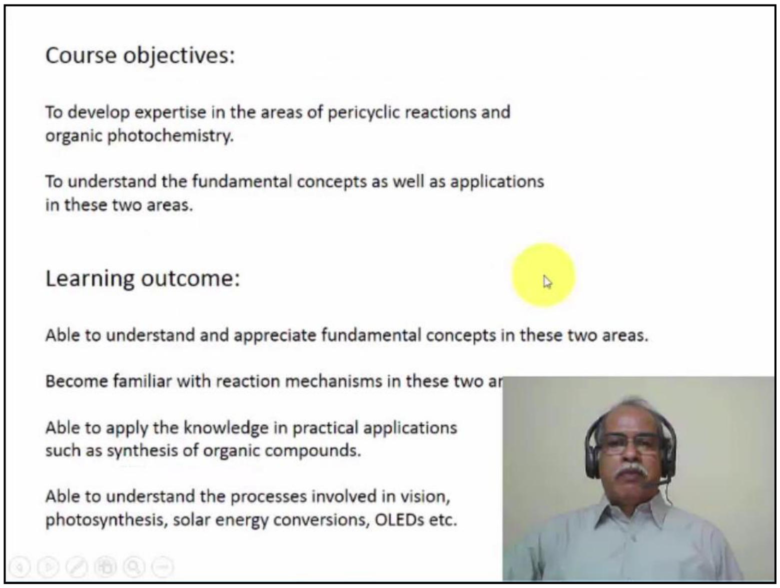

Before we go into that, let us see what are the course objectives. This course is essentially on two important topics namely, pericyclic reaction, and organic photochemistry. So, essentially going through this course, will make you an expert in these two areas. To understand the fundamental concept as well as the application in these two areas, this course is tailor made to cater the needs of the students. What are the learning outcomes of this particular course?

You will be able to understand and appreciate the fundamental concepts, in these two areas namely, pericyclic reaction and organic photochemistry. Become very familiar with the reaction mechanisms, of these two areas. And, be able to apply the principles and the reaction mechanisms, that they have studied, or gone through in the process of organic synthesis, or synthesis of organic compounds.

Be able to understand, the processes involved in certain processors like, vision, photosynthesis, solar energy conversion, and OLEDs. Photochemistry will help you understand, the fundamental concepts, involved in this important topic. We will see, some of these things, at a later stage in this module.

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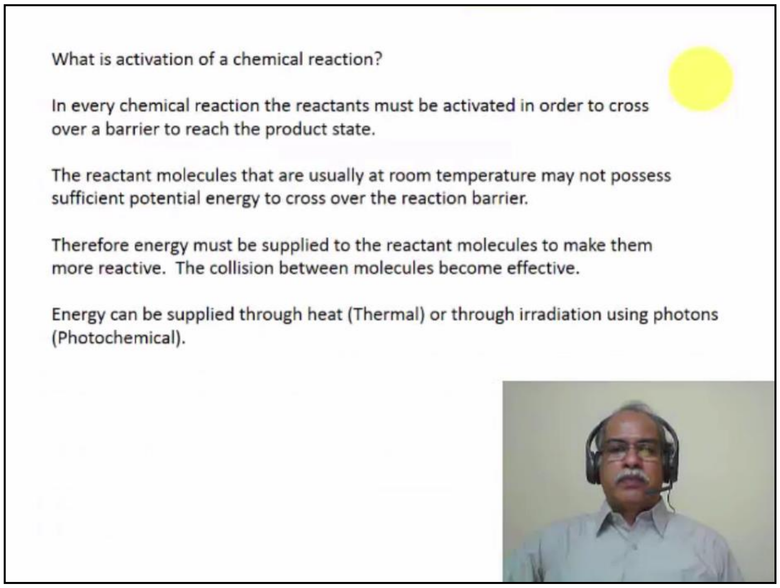

Now, what is an activation of a chemical reaction. You know that, certain chemical reaction takes place spontaneously, at room temperature. Some of them take place, even at very low. And some reaction needs to be given, some kind of an activation like heat or light, to be able to come over the barriers, that it possesses. Every chemical reaction, the reactant must have some activation, or it should be activated enough, to cross the barrier, so that it can reach the product straight.

And, this is essentially dictated by the transition state theory, or the activated complex theory, of the chemical reactions. The reactant molecules, that are usually at room temperature, may or may not possess sufficient potential energy, to cross over this barrier. In order to make them cross over this barrier, energy must be supplied to the reactants, to make them more reactive. In other words, the collision between molecules to become more effective, one needs to apply energy.

This application of energy can be done, either by simply heating the sample, which is a thermal methodology, or through the irradiation using ultraviolet visible light, for example, which would correspond to the photochemical processes.

So, these are the two fundamentally important process namely, for the activation of chemical reaction. One can either apply heat, or one can use photonic energy, to promote the chemical reaction. The pericyclic reaction has two components. One is thermally activated pericyclic reaction. The other one is photochemically activated pericyclic reaction. We will see several examples of the photo activation, as well as thermal activation of pericyclic reaction, during the course of this particular module, or subsequent modules, that may come in future.

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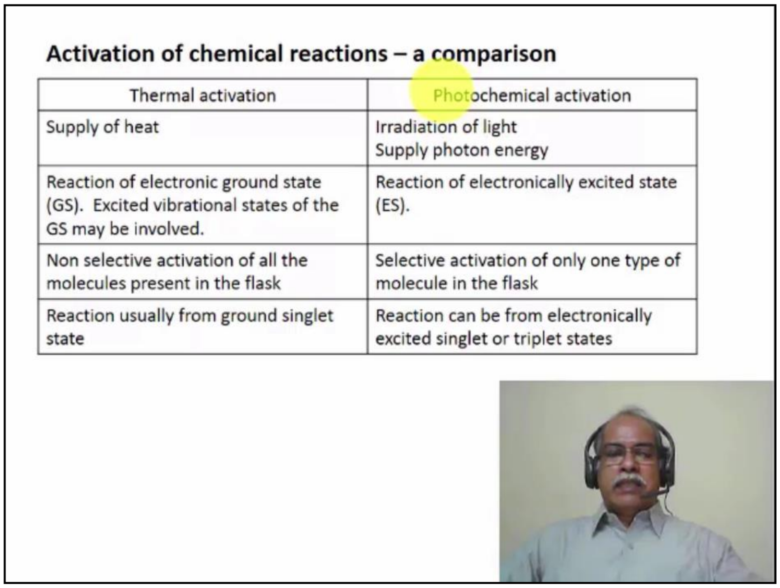

Now, what are the fundamental difference between, the thermal activation, and photochemical activation. This is listed, in this particular table. The difference is, in the case of the thermal activation, it is done by supplying of heat. In other words, by heating the reactants, one reaches the barrier, or overcomes the barrier of the chemical reaction. On the other hand, photo chemical activation is carried out, by irradiation through light. In other words, the photon energy is, what is supplied in the form of energy for the molecules, to overcome the barrier.

In the case of thermal activation, predominantly, the reactions proceed through the ground state electronic configurations. In other words, molecule exist on the ground state electronic configuration. Sometime, they may be excited to the vibrational levels, higher vibrational levels of the ground state, may be involved in the reaction. Nevertheless, they always proceed from the ground electronic state. Whereas, in the photochemical reaction, they applied photochemical energy, essentially promotes the electron, from the ground state to an excited state.

So, electronically excited molecule or atoms, are involved in the photochemical reaction. So, photochemical reaction essentially corresponds to reaction, coming from electronically excited state of the molecule. In the case of thermal activation, one cannot have a selective activation. Let us take an example of a diels-alder reaction. Where, diels-alder reaction involves, a diene reacting with a dienophile, to undergo the cyclo-addition reaction. So, there are two components involved. One is the diene, the other one is the dienophile.

Now, when we do the thermal activation of the diels-alder reaction, one cannot selectively heat, either the diene, or the dienophile. Because, they are in the same flask. So, one needs to heat the entire mixture. So, selective activation is seldom possible, in the case of thermal reaction.

Whereas, if you are doing a photochemical reaction, different molecules absorb a different wavelength of light. So, by choosing the proper wavelength of light, one can selectively activate, one or more molecules in the system. And, thereby selective activation, photochemical reactions is possible.

Let us take an example of two molecules. One is a colorless molecule. The other one is a red colored molecule. Suppose, one wants to activate the colorless molecule, it essentially absorbs the UV light. So, it can appropriately choose a UV wavelength, to excite that particular molecule, leaving the red colored molecule, un-activated. On the other hand, if one wants to activate the red colored molecule, one can do so, by choosing the wavelength corresponding to the red color of the compound, and thereby activating the particular compound alone, in a mixture of two compounds.

So, selective activation is a major signature of the photochemical reaction, which is not possible, in the case of thermal reaction. The case of thermal reaction, usually the ground state molecules exist, in the singlet state. So, the reaction takes place, from the singlet state of the ground state molecule.

On the other hand, photochemical reaction can take place, either from the singlet state, or the triplet state, depending upon the spin multiplicity of the state, electronically excited state, one can have reactions arising from, either the singlet state, or the triplet state of the molecule. So, these are the fundamental differences between the thermal activation, and photochemical activation, of chemical reaction. We will see, more of these examples, as we proceed through the modules.

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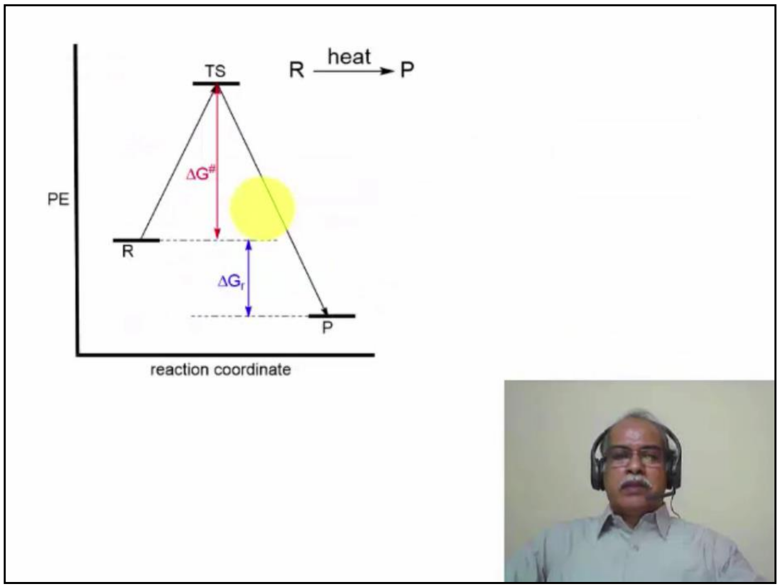

Now, this is a simple potential energy diagram, describing a reaction coordinate on the x-axis, and a potential energy in the y-axis, for example. The reaction coordinate is essentially the progress of the reaction. Suppose, if a bond is breaking, then this would correspond to the length of the bond, that is being breaking. Or, if a bond is being made in a chemical reaction, which is often the case, one can plot the progress of the reaction, as the bond length variation, when the bond is being formed in this particular case. Potential energy, of course, is the energy of the molecule, that we are dealing with.

We have reactant molecules at certain potential energy, and the product molecule at certain potential energy. In order for the reactant molecules to come to the product state, it has a barrier, which is represented by this red arrow, corresponding to the free energy of activation. In other words, unless the reactant molecules are sufficiently activated, to go to the transition state, one cannot reach the product state.

In other words, there is no possibility to directly come from the reactants state, the product state, without having to cross over the activation barrier. This is what is dictated by the transition state theory, as well as the, otherwise known as the activated complex theory. So, this corresponds to the transition state, or the activated complex of the reactant molecule, going through certain absorbing, certain energy, and going through this particular state, which is the transition state. Now, the overall change in the free energy of the molecule, is represented by the blue arrow.

This is a spontaneous reaction. In other words, Delta G is negative, because the product is at a lower energy state, compared to the reactants. So, overall there is a loss of energy, corresponding to Delta G being negative value. This is a reaction. Where, the reaction essentially goes to the product, without the involvement of any kind of an intermediate state. Only a transition state is involved. Such reactions are known as concerted reactions. Where, no intermediate stages are observed, during the course of the reaction.

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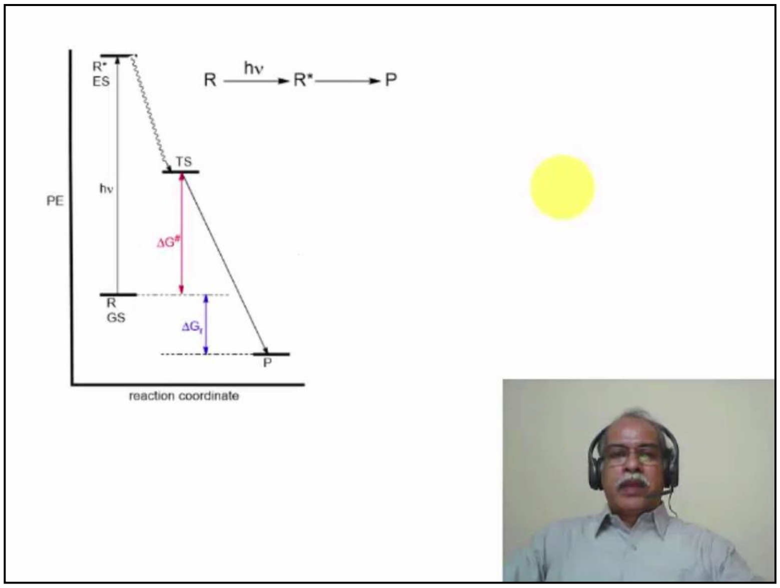

Now, this is a typical potential energy diagram, for a photochemical reaction. In a photochemical reaction, the ground state molecule initially absorbs certain photons of a definite wavelength, corresponding to the absorption of the molecule, or which is a reactant molecule. In doing so, it is electronically excited from the ground state to the excited state. R star represents an electronic isomer of the R.

In other words, the electron distribution in the ground state, and the electron distribution in the excited state, are different. So, they are basically electronic isomer, is what, we can refer to. And, once it reaches this particular state, the excited state, molecule will come back to the ground state, by means of relaxation. And, one of the relaxation is essentially losing energy to the surroundings, and reaching certain point, which corresponds to the transition state of the reaction.

And, once it reaches a transition state, it can go either to the starting material, or it can go to the product. Since, we are continuously irradiating the starting material, more and more of it will get excited. So, eventually, the entire process will be driven to the formation of the product, in the process. Once again, the Delta G is essentially the free energy of activation, of this particular reaction. And Delta G, R is the free energy change of this chemical reaction.

This is a chemical representation, equation wise representation, of the photochemical reaction. Initially, the reactant absorbs the photon, goes to an excited state, which is an electronic isomer of the ground state. From the excited states, undergoes many processes, including radiative, non-radiative processes, which we will see in detail, later. And, one of the path way it can take, is to go to the product, which is a chemical reaction. So, this is a absorption of light energy, followed by a chemical reaction, is what drives the photochemical reaction, in most instances.

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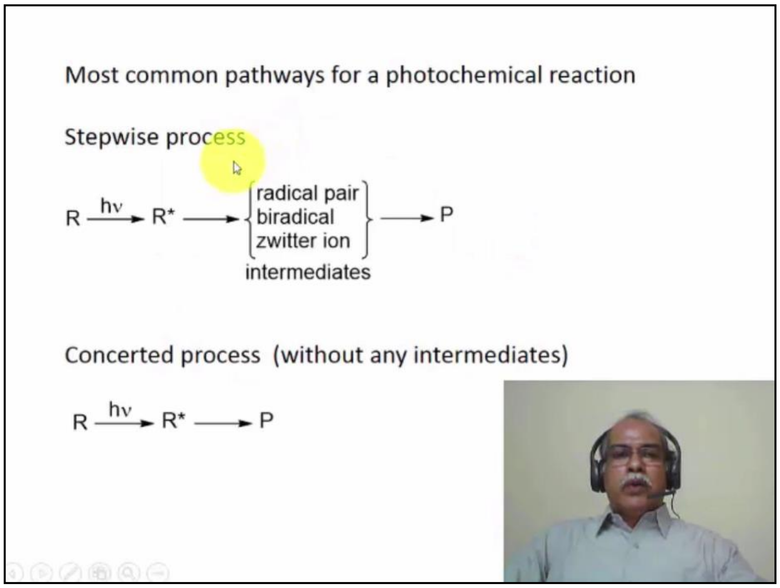

Now, the most common pathway for the chemical reactions. One can take a stepwise process, or one can take a concerted process. Essential difference between a stepwise process, and the concerted processes is, in the stepwise process, there are intermediates, that are involved here. Let us take this photochemical reaction. We already mentioned the starting material, or the reactant absorbs the photon, and goes to an electronically excited state.

From the electronically excited state, it can either dis-associate into a radical pair, or it can form a biradical, or it can form a zwitter ion. These are the intermediate stages of the chemical reaction. And, from this intermediate stage, a thermal process takes place, corresponding to the product formation. So, the electronically excited molecule, essentially losses energy in forming the reactive intermediate species.

And, from the reactive intermediate species, the product is being formed in this reaction. On the other hand, if you consider a concerted process, this is a process, where no intermediates are observed. Essentially, the reactant goes to the excited state. And, then goes to the product, directly. If it were to be a thermal process, the reactant will directly go to the process, through a transition state, instead of a excited state, for example.

So, that is also considered to be a concerted process. Now, when the reactant goes to the product, it can go through a radical pair, where two radicals are formed simultaneously, or it can form a biradical. Biradical is essentially, two radicals on the same molecule, at two different centers. If they are separated by n number of atoms, then you call it as, one n biradical. If it is separated by three carbon atoms, or three atoms in general, it will be one three diradical.

If it is separated by four atoms, it will be one four diradical, and so on. So, biradical is essentially two radical species, that is present in the same molecule, at different centers, separated by n number of atoms. Zwitter ions, of course are ions, where you have both the charges being present, + charge, as well as the – charge. And, these are essentially polar intermediates, that are formed during the course of the chemical reaction.

So, the photochemical reaction can essentially go through, any one of these radical mechanism, or a biradical mechanism, or a zwitter ionic mechanism, before it goes to the product. The point, that is covered in this particular slide is that, one can have chemical reactions, which are taking place through stepwise process involving intermediates, or the chemical reaction can also take place in a concerted manner, without the involvement of any kind of an intermediate. So, that is the message, that i want to convey, in this particular slide.

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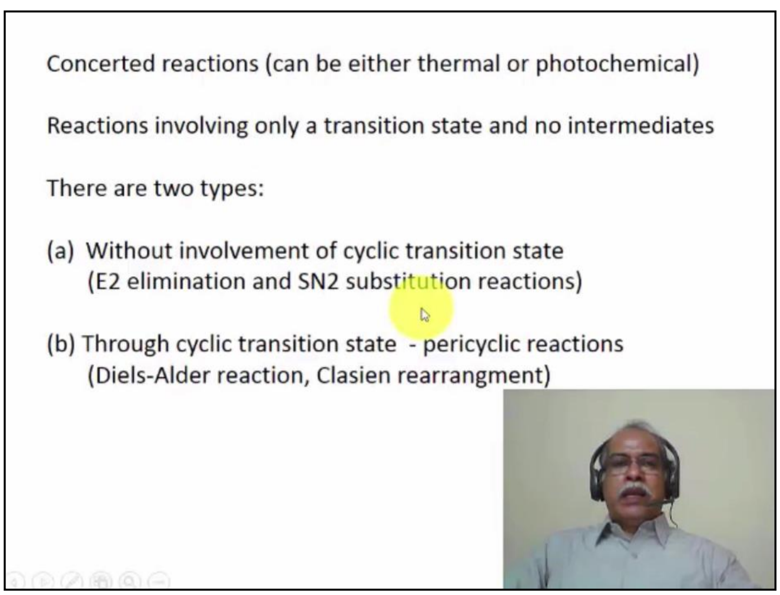

Now, the concerted reactions can be, either thermal reaction, or photochemical reaction. We have examples of concerted reaction, both under thermal, as well as photochemical condition. Now, coming back to the concerted reaction, these are reactions, which proceed through a transition state, without the involvement of any kind of intermediates. Both the thermal type, as well as photochemical type, concerted reactions are known. And, there are two types of concerted reactions.

Those reactions, which involve a cyclic transition state. And, those reactions, which do not involve, any kind of a cyclic transition state. So, whether the transition state is a cyclic transition state, or re-cyclic transition state, makes the classification of the two types of concerted reaction. The ones, that proceed through the cyclic transition states, are the one, that are known as pericyclic reactions. And, the ones, do not proceed through the cyclic transition states, are not pericyclic reaction.

The examples can be given, in the form of E2 elimination, and SN2 substitution reaction, which are concerted reaction. But, they do not proceed through a cyclic transition state. So, they will be just a normal concerted reaction. Whereas, reactions like diels-alder reaction, or claisen rearrangement, which proceed through a cyclic transition state, are known as the pericyclic reaction.

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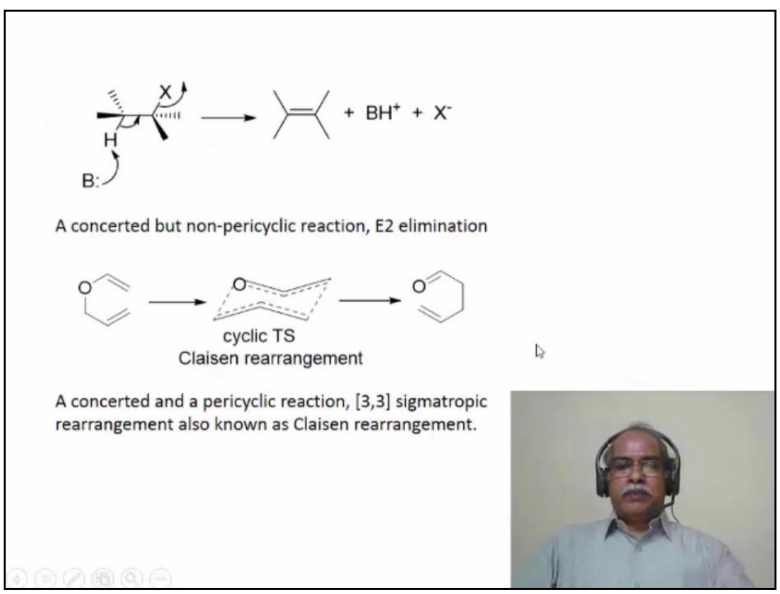

The example is illustrated here. Consider the reaction of an E2 elimination reaction, where the base abstracts this hydrogen, with a simultaneous loss of the halide, or the leaving group X minus going out of the molecule. Here, the CH bond breaking, as well as the CX bond-braking, take place simultaneously. That is why, it is a concerted reaction.

But, as you can see, the reaction mechanism does not involve, any cyclic structures, of transition state structures, of this particular elimination mechanism. So, this is a concerted reaction, but non-pericyclic type concerted reaction. Whereas, if you consider a claisen rearrangement reaction, the claisen rearrangement is essentially a rearrangement of an Allyl Vinyl Ether, into a Gamma Delta unsaturated carbonyl compound.

And, you can see here, it has to go through a cyclic kind of a transition state, in order to form a bond between these two carbon centers. If you follow the cursor, you understand the formation of this particular reaction. With the breaking of the carbon oxygen bond, and formation of a carbon-carbon bond, it proceeds through, a chair type of a transition state, cyclic transition state. And, that is why, this reaction is a pericyclic reaction.

Because, it proceeds through a cyclic transition state, and it is also a concerted reaction. These are the two necessary criteria, for turning a reaction, as a pericyclic reaction.

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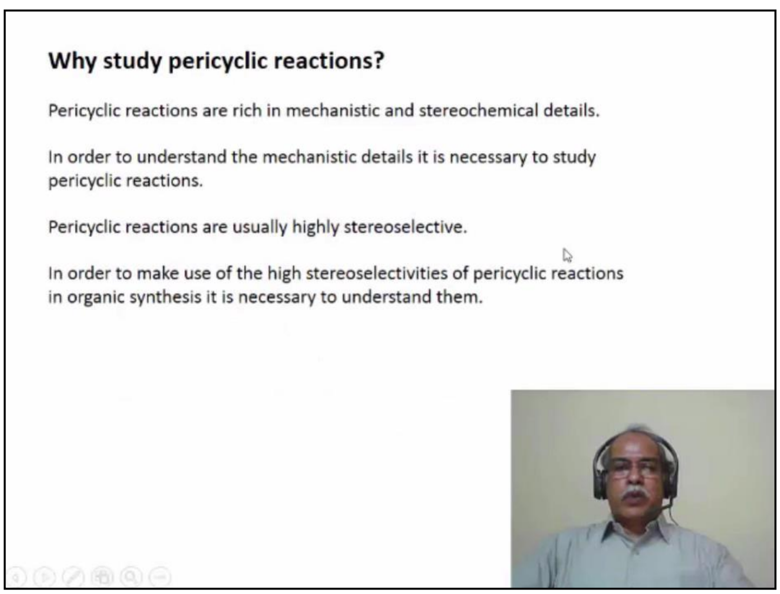

Let us move on. Now, why does one need to study, pericyclic reaction. Pericyclic reactions, once upon a time, were considered as, no mechanism reaction. Because, no intermediates could be found, in this reaction. People thought, this reaction do not have, any kind of a mechanistic details involved, in order to be, able to identify, reactive intermediates, and so on. However, pericyclic reaction, turns out to be the richest, and reaction mechanistic details, and stereo chemical details. In order to understand, the mechanistic details of this pericyclic reaction, it is necessary to study them.

Pericyclic reactions are extremely useful reactions, in organic synthesis. Because, they are highly Stereo-selective, and Regio-selective, in nature. So, the selectivities, that are involved in the pericyclic reaction is, what makes them very attractive, in organic synthesis. So, in order to make use of the high selectivities of the pericyclic reaction in organic synthesis, it is necessary to understand their reaction mechanism.

How they proceed? And, what kind of interactions take place, within the reactive molecule, and so on. So, this is what essentially drives one, to study the pericyclic reaction. There are quite a lot of pericyclic reaction, that will come across in due course. And, during the course of this pericyclic reactions, one will learn a lot of details of the mechanistic, as well as the stereo-chemical aspects.

So, some basic understanding of reaction mechanism, and stereochemistry of organic compounds, would be extremely helpful, in understanding the pericyclic reaction.

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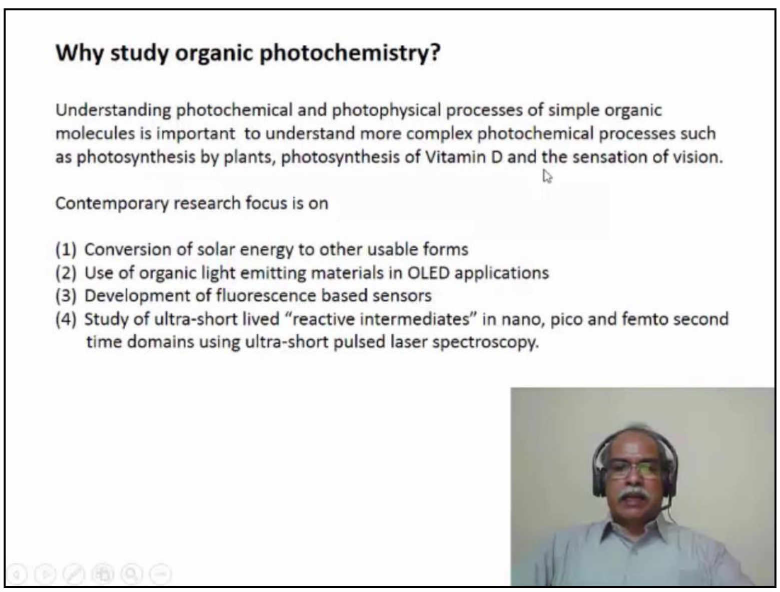

Now, why do we need to study, photochemistry? This is a question, that one needs to ask, before proceeding further. If you consider, important processes like the vision, in other words, the sight of seeing, something. There are some photochemical reactions, that are taking place in our eyes. And, these photochemical reactions are extremely simple reactions, happening in a fairly complex system, in the biological system. In other words, the simple organic molecules photochemistry, if you can understand properly, then one can extrapolate the processes, that are involved in simple organic molecules, in to larger complex biomolecules.

The sensation of vision, essentially is because of the molecule, called the retinal, which undergoes a cis-trans isomerization, that is triggered by absorption of a photon. So, if one understand the cis-trans isomerization process of a simple organic compound, then one should be able to understand, what is happening in the process of vision also. Similarly, for example, the synthesis of vitamin D, that occurs under our skin, for example.

When skin absorbs light, certain transformations take place in steroidal kind of molecule, which essentially leads to the synthesis of vitamin D, which we will see at a later stage, when we talk about the photochemical reaction. Photosynthesis by plants, for example, has been happening, ever since the earth was created. And, this photosynthesis, where the carbon dioxide is converted into sugar molecules, by means of absorption of light, using certain material like the chlorophyll, and so on.

The plants are able to do the photosynthesis, very efficiently. And, this is an important process. And, if one wants to understand, the electron transfer processes, that are involved in the photosynthesis, then basic photochemistry understanding is extremely important, to understand this complex molecules. Now, if you look at the contemporary research in photochemistry, these are the topics, that are listed here.

One is the conversion of solar energy, into useful forms of energy. In other words, conversion of solar energy into, for example, electrical energy, by means of photovoltaic cells. And, this is essentially conversion of photochemical energy, into electrical energy. And, what are the chemical reactions, that are involved in the conversion of a solar energy, into photochemical energy, one can understand, if one understand the basic concepts and reaction mechanisms, involved in organic photochemistry.

The use of organic light emitting materials, is happening quite often now. In fact, the cell phone displays, now you have the AMOLED display, which is amorphous material, organic light emitting diode material, is what is coated on the cell phone screens, to be able to have the colorful displays, that you will see in the cell phone. This is essentially an organic molecule, emitting light. Normally, photochemistry involves, the emission of light, after the absorption of photons. If certain molecules emit light, then we call it as emitting materials.

The emitting materials can be, either fluorescent emitting material, or phosphorus emitting material, depending upon, where the emission is taking place from. And, such materials, emitting materials, are what, are useful in the OLED application. In other words, photo chemists are the one, who developed the molecule, which are emitting light, and study the property of emission of light, by means of photon.

If the same process can be simulated, by means of applying electrical energy, then you have electroluminescence, which is responsible for the actual OLED application. So, the basis, or the fundamentals, of the OLED application, essentially originate from the photochemical research, in certain laboratories. For example, development of fluorescence-based sensors, another important aspect of photochemistry.

Here, fluorescent molecules are used for sensing applications, sensing toxic elements, like for example, mercury, cadmium, nickel, and so on, arsenic, and lead, and so on. These are fluorescence based organic molecules, where the fluorescence can be either enhanced or quenched, by the sensing application, that it is involved in. We will see a lot of examples, of this kind of fluorescence-based sensors, during the course of our lectures.

Finally, from the fundamental understanding of the photochemical processes, there is a topic called ultrashort laser spectroscopy. Where a short pulse of laser is being applied. Where the photon energy is being applied. And the reactive intermediates, that are formed is studied, in the very fast timescales of nanosecond, picosecond, or femtosecond, time scale.

Nanosecond is essentially, 10 to the power -9 second. Picosecond is, 10 to the power -12 second. And, femtosecond is, ten to the power -15 second. Such ultrafast processes are the reactive intermediates, that live only for such a short duration, can be easily studied by means of the laser spectroscopy. Some aspects of this also, we will see, during the course of our lecture.

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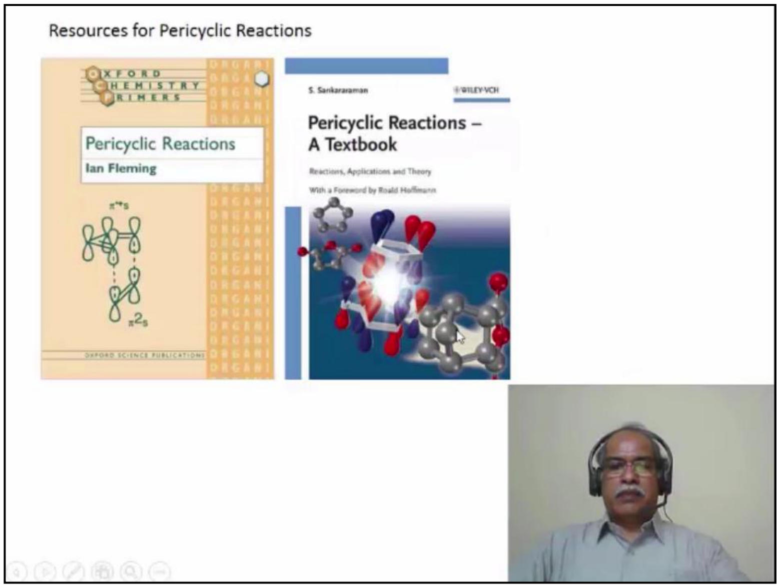

Now, the resource materials are given here. There are two books, that i would like to recommend, for the topic of Pericyclic Reaction. One is, Oxford Chemistry Primer on Pericyclic Reactions, by Ian Fleming. This is a thin book. It is a very nice book, to read and understand. And, i would recommend this particular book. One other book, written by me, on Pericyclic Reaction.

This is a textbook. And, this book essentially covers the reactions, their applications, and certain aspects of the theoretical aspects of the reactions, are also covered in this particular book. So, both these books will be extremely useful for this course. Most of the examples are taken from these two books, primarily from the book, that i have written in pericyclic reaction, as well as the book written by Ian Fleming. I have taken, some examples from this book also.

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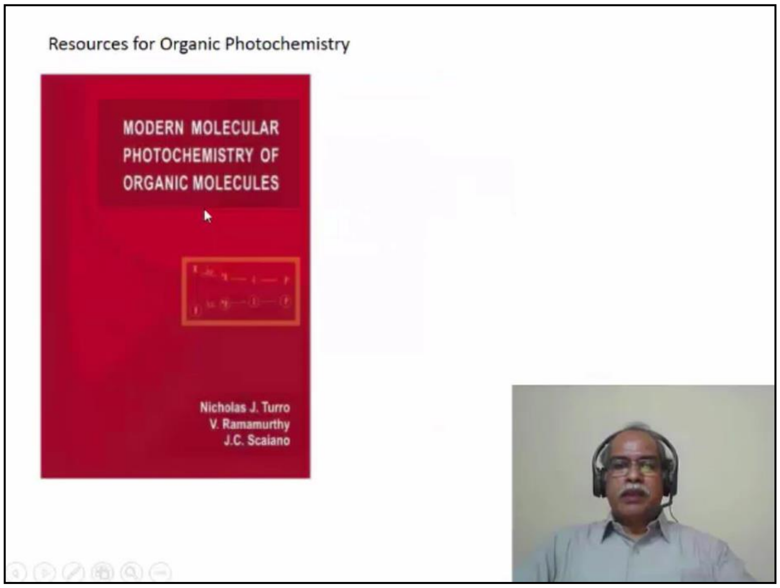

As far as photochemistry is concerned, organic photochemistry is concerned, the book written by Nicholas Turro, V Ramamoorthy, And J C Sciano, is an extremely useful book. This is one of the most more modern books, that are available in the organic photochemistry. The topic of the book is modern molecular photochemistry of organic molecules. Covers the theoretical aspects, as well as the reaction mechanism, and the practical aspects of organic photochemistry, is covered in this particular module.

So, during the course of the next few lectures, we will start with the pericyclic reaction. And then, finally go on to the organic photochemical aspects of photochemistry of organic molecules, we will cover at a later point. I hope, you enjoyed this particular module. And, i hope, you will enjoy the subsequent module also, that i would like to present, on the two topics of pericyclic reactions and organic photochemistry. Thank you very much, for your attention.