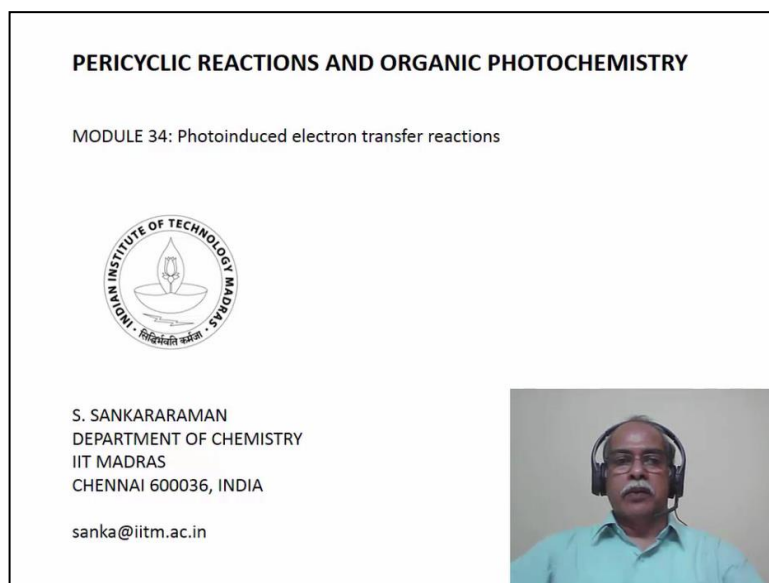


Pericyclic Reactions and Organic Photochemistry
S. Sankararaman
Department of Chemistry
Indian Institute of Technology, Madras


Module No. #08
Lecture No. #34
Photoinduced Electron-Transfer reactions

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PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 34: Photoinduced electron transfer reactions



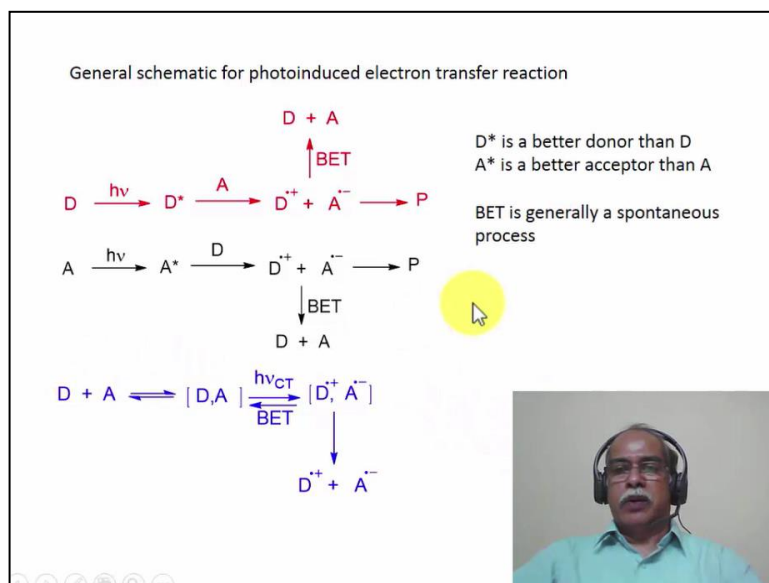
S. SANKARAMAN
DEPARTMENT OF CHEMISTRY
IIT MADRAS
CHENNAI 600036, INDIA

sanka@iitm.ac.in

Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. We are in Module Thirty-Four now. In this Module, we will consider a very important concept namely, Photoinduced Electron-Transfer reaction. When a molecule is excited, to its electronically higher excited state, it can do many things. It can get deactivated, to the ground state, by Emission, or Non- Emissive methods. It can, for example, be quenched by another molecule, to come back to the ground state.

It can also undergo, Electron-Transfer reaction, with a suitable substrate, with appropriate oxidation reduction potential. It can either donate an electron, if it is a Donor, or it can accept an electron, if it is an Acceptor. We will define, what is a Donor, and Acceptor, in a few minutes.

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But, we will consider, the various aspects of Photoinduced Electron-Transfer reaction, in this particular module. Now, let us consider, this particular scheme. In this scheme, what happens is, a Molecule-D, which is an abbreviation for Donor. Donors are typically, electron rich compound, like Aromatic compound, Olefin compound, Amines, and so on. When, it undergoes an excitation, by absorption of photon energy, it goes to the higher excited state.

From the higher excited state, when it encounters another molecule, which is an Electron-Acceptor, which is deficient in electron, there is an Electron-Transfer process, that takes place. In other words, from the neutral Donor excited state molecule, an electron is transferred on to the Acceptor molecule. And, since both of them, are to start with neutral molecule, when an electron is transferred, you produce a radical. When the electron is transferred, you produce a charge also.

So, what you produce, is a charged radical. In the case of Donor, it produces the Cation radical. In the case of an Acceptor, it produces the Anion radical, by accepting an electron from the excited state Donor. Now, the Donor-Acceptor Radical Ion-Pair, is what is usually produced, initially. Then, it diffuses into free ions into solution, depending on the Solvent-Polarity. One of the factors, that will favor the Electron-Transfer process, rather than an Energy-Transfer process, is Solvent-Polarity.

Electron-Transfer process, typically is favored by solvents of high polarity, like for example, DMSO, Acetonitrile kind of solvents, are useful for producing ion radicals, by Photoinduced Electron-Transfer reaction. Once, the ion radicals are produced, now they are free to undergo, two types of reaction. One, they can undergo Chemical reaction, to go to the product. There are several different types of Chemical reactions, these ion radical pair, can undergo, to go to the product

Or, they can simply undergo a Back-Electron-Transfer, abbreviated as BET. Back-Electron-Transfer, in which case, the Acceptor Anion radical, donates back an electron to the Donor Cation radical, and it produces the Donor and Acceptor in the process, by wasting the energy of the photon, that is observed. So, Back-Electron-Transfer, is always an energy wasting process. Because, it reproduces the starting point from the Donor and Acceptor, is being reproduced, in this particular instance. The energy using process, is the product formation.

We will see, many examples of such reaction. Now, in the second scheme, what we have is, instead of a Donor, an Acceptor molecule is excited. And, from the excited state Acceptor molecule, an electron is being accepted from the Donor, when it encounters an electron rich molecule. And, in the process of donation of an electron, the Donor becomes the Cation radical. And, by process of absorbing the electron, the Acceptor becomes the Anion radical.

The Donor-Acceptor Anion radical, Cation radical, that is produced, can go to the product, by means of Chemical reaction. Or, it can simply undergo, the Back-Electron-Transfer reaction once again, in terms of producing the Donor and Acceptor back, which is an energy wasting process. So, there are two types of Electron-Transfer process, that we have seen. One is in which, the electron rich compound is excited, to the higher excited state. Another one, Electron poor compound is excited, to the higher electronic excited state.

In addition to that, there is another process. The Donor and Acceptor molecules, can form a ground state, Charge-Transfer complex. The DA, written within the square bracket, essentially represents a Charge-Transfer state. So, the Donor-Acceptor in the ground state itself, it forms a Charge-Transfer complex. Charge-Transfer complexes are finite species, with definite spectroscopic absorption bands, for example, which is not present in, either the Donor, or in the Acceptor.

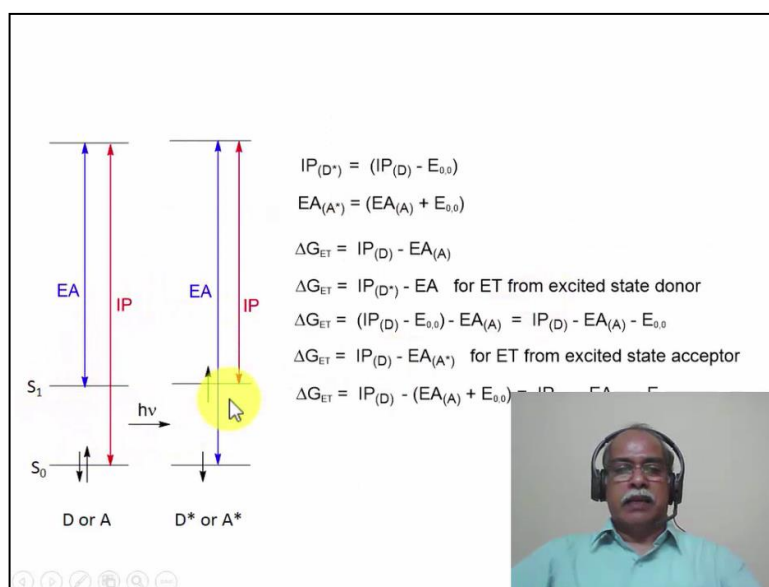
When you mix a Donor, and an Acceptor, usually the Charge-Transfer band is formed, along with a Charge-Transfer complex, in solution. A typical example would be, the solution of Iodine in Benzene, for example, is purple in color, because of the Charge-Transfer band, associated with the Benzene Iodine complex.

Alternatively, if you take a, colorless solution of Naphthalene rich molecule. Tetracyanoethylene, is an electron deficient molecule. When you mix some together, you get vivid colors, because of the formation of the Donor-Acceptor complex, which is corresponding to the Charge-Transfer band. When the wavelength of excitation, corresponds to the Charge-Transfer band, Electron-Transfer takes place from the Donor, to an Acceptor, producing the charged Cation radical, Anion radical pair. Within the solvent cage, this is formed. So, they are called, Contact Ion-Pairs.

This is according to the, Mulliken's theory of Charge-Transfer excitation. The specific excitation in the CT band, allows the transfer of an electron from the Donor, to Acceptor, to take place. And here, there is no excited state Donor, or excited state Acceptor, involved in the process. Directly, the Donor Cation radical, and the Acceptor Anion radical, is produced. This, of course, can diffuse into the solution, to free ions, from which, Chemical reactions can take place. Or, it can undergo, spontaneous Back-Electron-Transfer, to produce a Charge-Transfer complex, or the Donor and Acceptor.

So, the Back-Electron-Transfer can take place, by collision between these two, or within the radical Ion-Pair, it can undergo the Back-Electron-Transfer process. Now, any molecule in the excited state, is a better Donor, as well as a better Acceptor. This can be easily rationalized, by means of an Energy Profile diagram. The Back-Electron process, is generally a very spontaneous process. This also, we will see in a minute, by means of an Energy Profile diagram. Let us now carefully consider, this energy diagram.

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This is the, either the Donor, or Acceptor, does not matter. We can define, a Donor and Acceptor, only with respect to each other. So, let us consider, this particular diagram here. This is the ground state, electronic configuration of the molecule. The two electrons, are in the S_0 state, for example. This is a highest occupied molecular orbital. This is the first, singlet excited state of this molecule.

Now, if you want to define two parameters, which are important in defining, the Donor-Acceptor properties of a molecule, these are the Ionization-Potential, and Electron-Affinity. Ionization-Potential, essentially tells you, how easy it is to remove an electron, from the highest occupied molecular orbital, to infinite level, which is the vacuum level, which is this

particular level, here. So, the energy that is required, to be put in the molecule, to excite the electron from the S_0 state, to the vacuum level, is what is known as Ionization-Potential.

Higher, the Ionization-Potential, it is difficult to ionize the molecule. Lower, Ionization-Potential means, it is easier to ionize the molecule. On the other hand, this Blue Gap, that is shown here, between the vacuum level and the S_1 level, is the Electron-Affinity. It is an energy, that one needs to put in, in order to accommodate an electron, in the S_1 molecular orbital of the Donor or Acceptor, for example. So, this is an Electron-Affinity. And, this is an Ionization-Potential.

Now, let us see, what happens, when we excite the molecule. We can excite, either the Donor or Acceptor, does not matter. We do not have to define it, at this stage. Excitation process, essentially promotes this electron, to the higher electronic excited state. So, there is 1-Electron in the S_0 state, and 1-Electron in the S_1 state, now. Now, if you look at the Ionization-Potential, the Ionization-Potential energy is now reduced. In other words. It is reduced by a quantum of this Gap, which is supposed to be the, E_{00} Gap.

E_{00} , signifies the Gap between, the 0-Vibrational level of the S_0 state, and the 0-Vibrational level of the S_1 state. So, the Ionization-Potential, is now reduced. In other words, the molecule is easier to ionize, in the excited state, compared to the ground state. So, the molecule is a better Donor, in the excited state, compared to the ground state. And, this is what is meant by, the Donor is a better Donor, in its excited state, than in the ground state.

Similarly, an Acceptor is a better Acceptor, in the excited state, than in the ground state. Now, if you look at the Electron-Affinity of the molecule, this would correspond to the Electron-Affinity of the molecule.

The Electron-Affinity, in fact, corresponds to the energy, that is necessary to put the electron in this shell, and not in this particular shell. Whereas, the Ionization-Potential, corresponds to removing the electron from this shell, to the infinite, or the vacuum level.

So, the Electron-Affinity, actually is increased for the molecule. So, in the excited state, the molecule has a better Electron-Affinity, which means, it is ready to accept electron, even better in the excited state, compared to the ground state. So, let us make the statement. An organic molecule, in its excited state, is a better Donor, as well as a better Acceptor. Now, Ionization-Potential of the excited state molecule, is nothing but the, Ionization-Potential of the ground state, minus the E_{00} , which is this particular Gap.

In other words, the Ionization-Potential, plus the E_{Z-0} of the molecule, corresponds to the Ionization-Potential, in the ground state. So, this expression can be easily understood, if you follow this diagram. Similarly, the Electron-Affinity of the excited state molecule is, the

Electron-Affinity in the ground state, plus the E_{00} value, which is this particular Gap, that corresponds to the Electron-Affinity in the excited state.

So, the Electron-Affinity is higher, in the excited state, the Ionization-Potential is lower, in the excited state of a molecule, which makes it a better Donor, as well as a better Acceptor. Now, in order to identify, the process of Electron-Transfer, we have to define certain parameter like, the free energy of activation, for the Electron-Transfer process. In the gas phase, typically, the free energy of activation for the Electron-Transfer process, is nothing but, the difference between the Ionization-Potential of the Donor, minus the Electron-Affinity of the Acceptor.

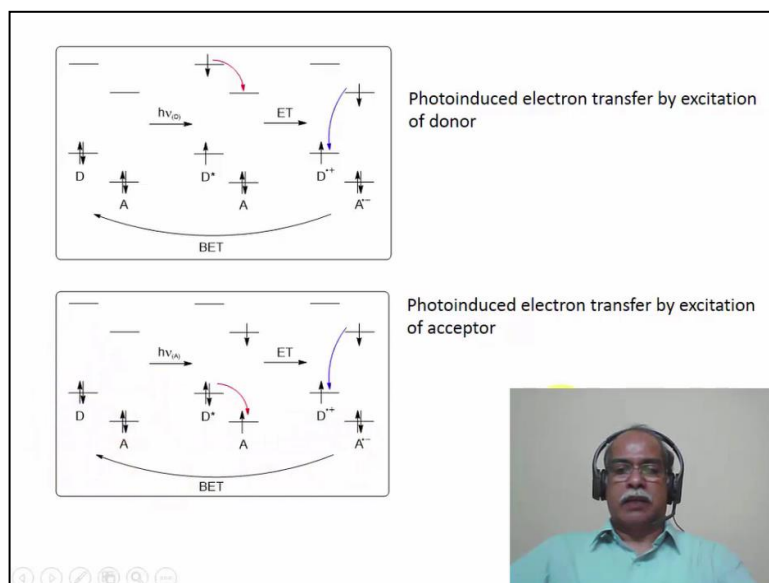
Now, if it is an excited state electron process, where the excitation is from the excited state Donor, the Electron-Transfer is taking place from the excited Donor, then you have to substitute the Ionization-Potential of the excited state Donor, in the place of the Ionization-Potential of the ground state Donor. Because, this is coming from, this process. Donor is excited first, and then the Electron-Transfer process, is taking place.

So, in the Photoinduced Electron-Transfer process, where the Donor is excited, the Ionization-Potential of the excited state Donor, is what matters. And, if you substitute the Ionization-Potential, corresponding to this value here, Ionization-Potential of the excited state Donor, is nothing but, the ground state Ionization-Potential, minus E_{00} . So, that is the expression, that one gets. So, this is an expression, that one uses for calculating the free energy change, associated with the Electron-Transfer, when the Donor is getting excited.

Similarly, when the Acceptor is getting excited, for example, the Electron-Affinity of the excited state Acceptor, is what is used. And, this expression is what is true, for the Electron-Affinity of the excited state Acceptor. It is, Electron-Affinity of the ground state, plus the E_{00} . So, that corresponds to this expression, which corresponds to the Electron-Transfer free energy change of the Electron-Transfer, when the Acceptor is excited, to the corresponding electronically excited state.

So, these equations are important, to understand. These equations, essentially arise from this diagram, in terms of defining the, excited state Donor Ionization-Potential, and Acceptor Electron-Affinity, and so on. The overall free energy change for the Electron-Transfer process, is what is given, in these expressions. Now, let us try to understand, how the Electron-Transfer process, take place.

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First, the Photoinduced Electron-Transfer, by the excitation of the Donor, we will consider. Now, a Donor is a one, which is easier to ionize, compared to an Acceptor. So, the Ionization-Potential, in other words, the Homo level, as well as the Lumo level of the Donor, will be at higher level, compared to the Acceptor. Acceptor has a larger Electron-Affinity. So, this is the larger Electron-Affinity, compared to this one, here. So, the energy levels are placed appropriately, to define the Donor and Acceptor.

A molecule can be a, Donor or Acceptor, depending upon, what is the counterpart. In other words, whether the Ionization-Potential of the counterpart is higher, or the Electron-Affinity of the counterpart is higher, makes its Donor and Acceptor, with respect to each other. So, i hope, you understand this diagram, being drawn in this particular manner, where the Homo level of the Acceptor, is lower than the Homo level of the Donor. Similarly, the Lumo level of the Acceptor, is lower than the Lumo level of the Donor.

Now, what happens in the electronic excitation, takes place for the D, the electron is excited from this level, to the higher level. So, this is a, electronic configuration of D-Star, now. Once, you have this electronic configuration, there is a direct downward jump of the electron, into the Acceptor Lumo level. In other words, this is a highly Exothermic reaction, that is why, this reaction is fairly spontaneous. So, after the Electron-Transfer takes place, the Donor loses an electron, so it becomes a Cation radical. The Acceptor gains an electron, so it becomes an Anion radical.

So, this would be the electronic configuration of the, Donor Cation radical, and the Acceptor Anion radical. Now, the Blue arrow indicates, the transfer of electron, from the Anion radical of the Acceptor, to the Donor, which will essentially produce back, the starting point. So, you

can see here, in fact, the exothermicity, or the spontaneity, of the Forward-Electron-Transfer, is not as much, compared to the Back-Electron-Transfer.


The Back-Electron-Transfer, has a much higher driving force, compared to the Forward-Electron-Transfer, in terms of the Electron-Transfer processes, that are defined. Similarly, one can also define, the Electron-Transfer process, when the Acceptor is excited. So, in this case, the Acceptor is the one, that gets excited. So, the Electron-Transfer is taking place, from the S₀ level of the Acceptor, to the S₁ level of the Acceptor.

This is an electronic configuration, of the excited state Acceptor. Sorry, this should be excited state Acceptor, and ground state Donor, there is a mistake here. Once, you have the excited state Acceptor, now this is a spontaneous process, of Electron-Transfer from the Donor, to the Acceptor, producing the Donor Cation radical, and the Acceptor Anion radical. You can, once again see the Back-Electron-Transfer, is represented by the arrow, which is Blue arrow here.

This is also a spontaneous process. In fact, this is more spontaneous, than the Forward-Electron-Transfer process. The Back-Electron-Transfer energy wasting process, essentially produces a starting material back, by means of a transfer of electron from the Anion radical of the Acceptor, to the Cation radical of the Donor. Now, the important parameter, for the sensitizer.

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| Sensitizer | energy of S ₁ (eV) | Reduction potential (eV) vs SCE |
|-------------------------------|-------------------------------|---------------------------------|
| 1,4-dicyanobenzene | +4.27 | -1.60 |
| 1,2,4,5-tetracyanobenzene | +4.10 | -0.66 |
| 1-cyanonaphthalene | +3.88 | -1.98 |
| 1,4-dicyanonaphthalene | +3.45 | -1.28 |
| 9-cyanophenanthrene | +3.50 | -1.92 |
| 9-cyanoanthracene | +3.10 | -1.13 |
| 9,10-dicyanoanthracene | +2.86 | -0.89 |
| 2,6,9,10-tetracyanoanthracene | +2.82 | -0.45 |
| N-methylacridinium salt | +2.75 | -0.43 |
| Chloranil | +2.40 | +0.02 |



Sensitizer, is nothing but a compound, which observes initially, the electron energy of the photon, and in turn, it transfers the electron to the Acceptor or Donor, depending upon, whether we are defining the sensitizer, as an Acceptor or a Donor. What are the important parameters for a sensitizer, is a singlet higher excited state energy, which will define the E-00

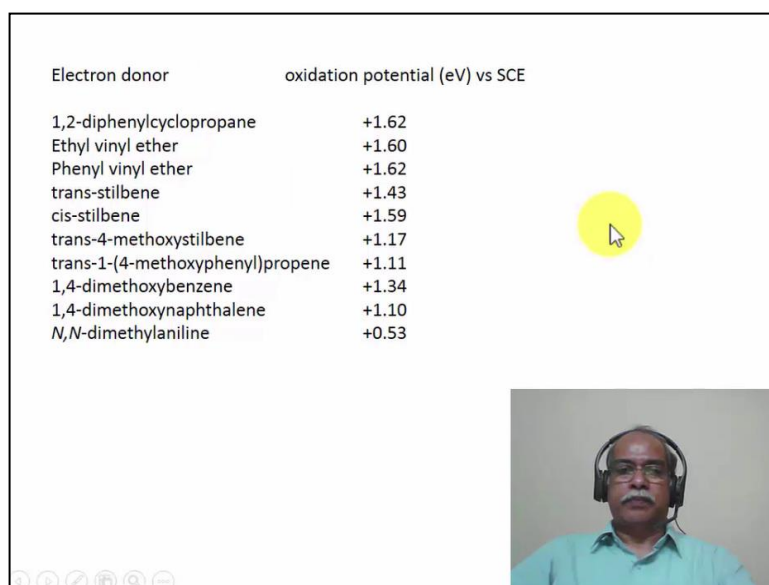
value, for example. In other words, in this expression, the E-00 correspond to this particular Gap.

And, is the same Gap, that is mentioned here as a, S1 level energy, compared to the ground level, which is a 0-Level, for example. The other parameter, that is important, as far as the sensitizer is concerned. These are all, Electron-Acceptor sensitizers. So, the reduction potential, is extremely important. This is obtained from, the Electrochemical experiment. This is obtained from, the spectroscopic measurement of the, absorption spectrum of the molecule.

And, these two parameters, can be experimentally easily obtained, by means of Electrochemistry, as well as Spectroscopy, respectively. The Electron-Donors are molecules, which have a higher electron density.

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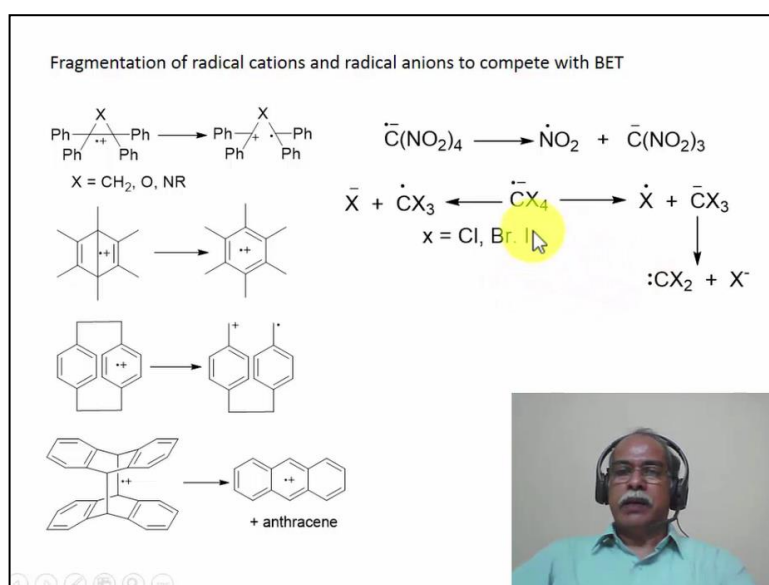
| Electron donor | oxidation potential (eV) vs SCE |
|----------------------------------|---------------------------------|
| 1,2-diphenylcyclopropane | +1.62 |
| Ethyl vinyl ether | +1.60 |
| Phenyl vinyl ether | +1.62 |
| trans-stilbene | +1.43 |
| cis-stilbene | +1.59 |
| trans-4-methoxystilbene | +1.17 |
| trans-1-(4-methoxyphenyl)propene | +1.11 |
| 1,4-dimethoxybenzene | +1.34 |
| 1,4-dimethoxynaphthalene | +1.10 |
| <i>N,N</i> -dimethylaniline | +0.53 |



Typically, Aromatic compounds, Olefins, and Amines, are the Electron-Donor. Ethers can be Electron-Donors, for example, because of the Oxygen lone pair. And, the parameters, that potentially important for the Electron-Donor, is oxidation potential, which is highly positive, in the case of Electron-Donors. We can see, these are highly negative, in the case of Electron-Acceptors.

So, these are the parameters, which are extremely important, for defining the Electron-Donor-Acceptor process. Now, once the Electron-Transfer takes place, in order to avoid the Back-Electron-Transfer, you have to consume, the Donor Cation radical, and the Acceptor Anion radical. Some of the Cation radical, and Anion radicals, are spontaneously decomposed, during the course of the Electron-Transfer process.

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And, such a decomposition, will ensure the return Electron-Transfer, or the Back-Electron-Transfer, is suppressed. So, it is advantageous to have productive photochemistry, by fragmenting the Cation radical, or Anion radical, to compete with the energy wasting Back-Electron-Transfer. These are some molecules, which will undergo, spontaneous Sigma bond fragmentation. Epoxides, and Cyclopropyl derivatives, Aziridine derivatives, for example.

These are all examples, where the 3-Membered ring strain is released, by breaking this Carbon-Carbon bond, to produce a corresponding radical, and the cation center, as distinct centers, [1,3] centers, [1,3] relationship of the cation, and the radical centers, in these molecules. Hexamethyl Dewar Benzene, for example, upon oxidation, gives the Cation radical. The Cation radical is highly unstable. It spontaneously, rearranges to the Aromatic Cation radical, which is the, Hexamethyl Benzene Cation radical.

Similarly, [2,2]-Paracyclophane is oxidized, to the corresponding Cation radical. Because of the ring strain, associated with this molecule here, the two Benzene rings are essentially, parallel to each other. And, the distance being about, 3.5 Angstroms or so. This is a highly-strained molecule. So, the strain is released by, breaking this Carbon-Carbon bond, to produce the Benzylic cation, and the Benzylic radical, which are stable, at this particular configuration. This is nothing but, the Photodimer of Anthracene.

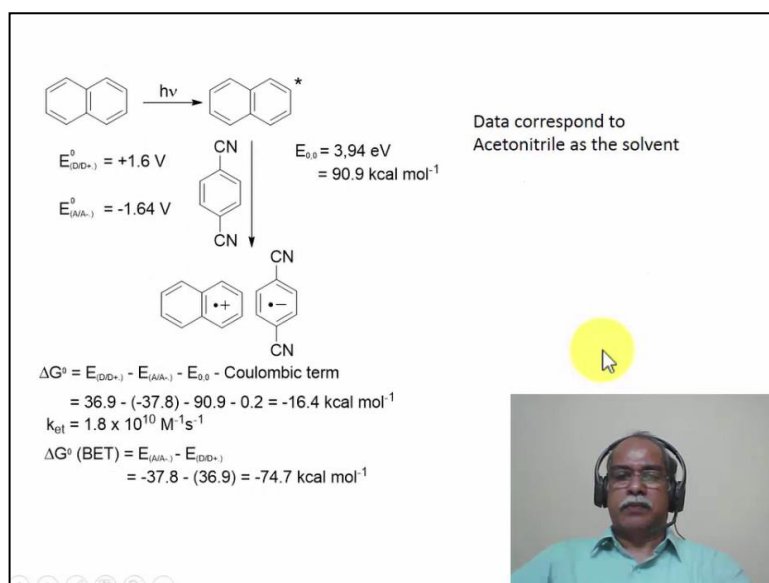
Photodimer of Anthracene, when it is oxidized by, Photoinduced Electron-Transfer to the Cation radical, these two Sigma bonds are cleaved, you get two molecules of Anthracene, one as a Cation radical, the other one as a free Anthracene. So, these are all examples of Cation radical, undergoing fast fragmentation process, that competes with the Back-Electron-Transfer process.

In the case of anion radicals, Tetranitromethane is a very classical example of an Anion radical, which spontaneously fragments to the Trinitromethide anion, and NO₂ radical, for example. The reaction rate is, so much so that, you do not see the species, even in the Femtoseconds spectroscopy. Femtosecond is 10⁻¹² seconds. This is shorter lived than, 10⁻¹² seconds.

So, this spontaneous process of fragmentation, ensures the Back-Electron-Transfer, being suppressed in the system. Similarly, Tetrahalomethane anion radicals also, spontaneously fragment, either a Trihalomethyl radical and Halogen anion is produced, or a Halide radical and the Trihalomethyl anion is produced. It depends on, whether it is Chlorine, Bromine, or Iodine. If it is a Chlorine kind of a molecule, this process is quite facile.

If, it is Bromine and Iodine, this process is also facile, for example. Once the Trihalo anion is produced, it further eliminates the Halide ion, to produce Dichlorocarbene, Dibromocarbene, and Diiodocarbene, for example. This is a classical way of producing the Dihalocarbenes, by means of reducing the Tetrahalomethane, to the corresponding Anion radical, and then fragmenting it to the, Dihalo species.

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Here is an illustrative example of, how to calculate, the free energy change, associated with the Electron-Transfer process. The Ionization-Potential, is in the gas phase. If you are going to measure, in the solution phase, the equivalent parameter is the, electrochemical oxidation potential of the Donor, for example. Whereas, in the case of the Electron-Affinity, that is applicable to the gas phase. In the solution phase, it is the Redox potential, or the reduction potential of the Acceptor, is what is important.

So, this Redox couple, Acceptor-Acceptor Anion radical, Redox couple reduction potential, can be measured, from the electrochemistry of the, let us say, the Dicyanobenzene, which is an electron deficient molecule, here. In the case of the Naphthalene, which is an electron rich molecule, the oxidation potential can also be measured. It is 1.6 Volt, for example. +1.6 Volt, with respect to, Saturated Calomel electrode. This is -1.64, with respect to the, Saturated Calomel electrode.

Now, the Naphthalene is excited, to a higher excited state of Naphthalene. And, the S1 energy, corresponds to 3.94 electron Volts. In other words, the E-00 value, the 0-Vibrational level of the S0 state, to the 0-Vibration level of the S1 state, corresponds to 3.94 Electron Volt, which is roughly 90.9 Kilocalories per mole, in terms of the unit conversion taking place, with the corresponding multiplication factor. This data, corresponds to, Acetonitrile as a solvent.

That is important. Because, the overall Electron-Transfer process, in a solution phase, is the oxidation potential of the Donor, minus the reduction potential of the Acceptor, minus the 00-Energy of the excitation wavelength, corresponding to the 00-Energy, is what is implied. And, finally, because of the ion radicals are being produced, a Coulombic term also comes into picture, which essentially takes care of the ionic interaction, between the Cation radical and Anion radical, that is produced here.

In the case of Acetonitrile, the Coulombic term is fairly small. It is about, 0.2 Kilocalories per mole. Now, this can be converted into, Kilocalories per mole. This also, can be converted into, kilocalories per mole. So, the E-Oxidation of the Donor is about 36.9, the E-Reduction of the Acceptor is about 37.8 Kilocalories per mole, for example. The E-00 is calculated as, 90.9 Kilocalories per mole. The Coulombic term, turns out to be, 0.2. Overall, if you calculate these parameters, it is about -16.4.

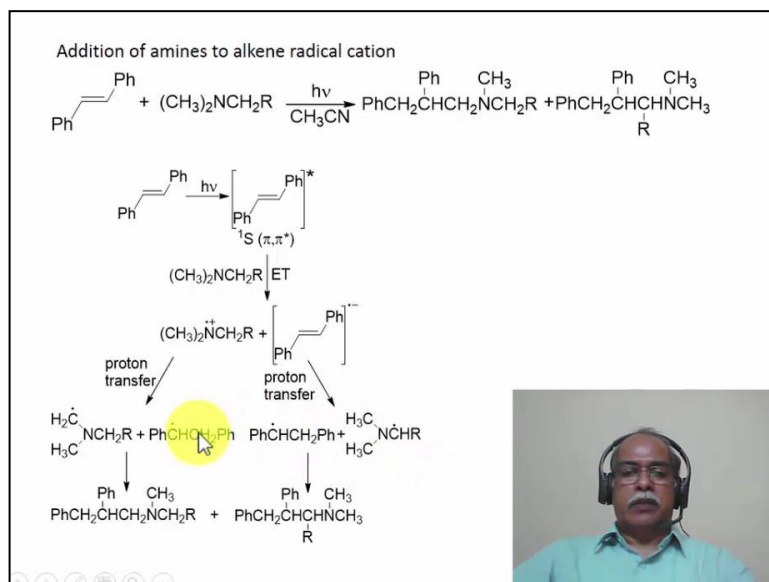
In other words, the free energy of Electron-Transfer is -16.4, indicating that, it is a spontaneous process. If you want to calculate, the Back-Electron-Transfer, now you have to take the electron oxidation potential of the Anion radical, which is nothing but, the reduction potential of the anion itself, in the negative sense. And, the Reduction potential of the Cation radical, which is nothing but, the oxidation potential of the neutral Donor. In other words, this is reversed, in the case of the, Back-Electron-Transfer.

So, that is becoming, even more highly spontaneous. The Delta-G, for the Forward-Electron-Transfer, which is this Electron-Transfer process, is only -16, it is spontaneous enough. But, the Back-Electron-Transfer, is even five times much more spontaneous, than the Forward-Electron-Transfer. That is one of the reasons, one need to suppress, the Back-Electron-

Transfer. Because, otherwise, there will not be any productive photochemistry, associated with the Photoinduced Electron-Transfer process.

Now, let us look into, some beautiful examples of reactions, which are carried out by, initial Photoinduced Electron-Transfer process.

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If you take Stilbene, and treat it with Tertiary Amine, and photolyze it. In other words, the photolysis wavelength, corresponds to the Stilbene absorption wavelength, in Acetonitrile, as a process. The Amine, splits into two, in terms of adding across the Carbon-Carbon double bond, producing these Tertiary Amines, in the process of, in other words, the Amine is added to the double bond, to produce these two compounds, in this. How are these two compounds produced? That is explained, in this mechanistic feature, here.

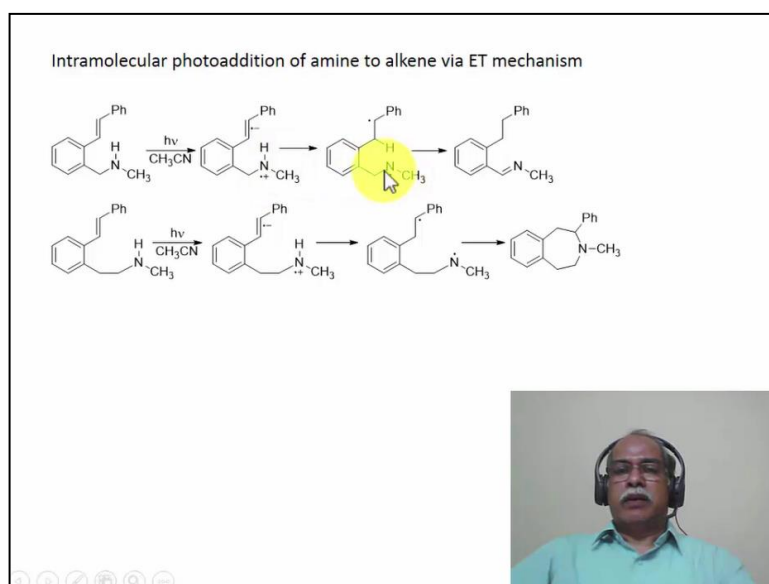
Stilbene is excited, to the corresponding higher excited state, singlet excited state, which is a PI-PI-Star excited state. In the PI-PI-Star excited state, it is an excellent Acceptor, because Amine is an excellent Donor, compared to this one. So, it accepts the electron, for example, from the Amine, to the excited state of the Stilbene, producing the Stilbene Anion radical, and the Cation radical of the Amine. Now, Proton transfer can take place, from the Methyl group, or from the CH2 group.

If, the Proton transfer takes place, from the Methyl group, to the Anion radical of Stilbene, you will produce the corresponding Benzyl radical, as well as the CH2 radical, attached to the Nitrogen, for example. On the other hand, if the Proton transfer is taking place, from the CH2 group, then you will produce the corresponding CHR, and the Benzyl radical, which is same as the Benzyl radical, coming from here. Please, try to understand, these are charged radical species. And, when they lose a Proton, they become radical.

In other words, the charge is transferred from, in the form of Proton, from here to here. So, as a result of that, the negative charge disappears, when the radical is produced. Since, the Proton is removed from the Cation radical, the resulting species is a radical species. Now, the radicals can recombine, to give Tertiary Amines, that are shown, as the product. This C, and this C, can recombine, to produce this molecule.

Similarly, this C, and this C, can recombine, to produce this molecule. Since, these are happening probably in a solvent cage, solvents separation does not take place. As a result of that, this combination, for example, this two Carbon centered radical combination, to produce the Hydrocarbon, does not take place efficiently. Because, it has to come out of the solvents shell, in order to meet this partner, and that does not take place readily. Only, these Tertiary Amine products are formed, during the course of the Photoinduced Electron-Transfer process.

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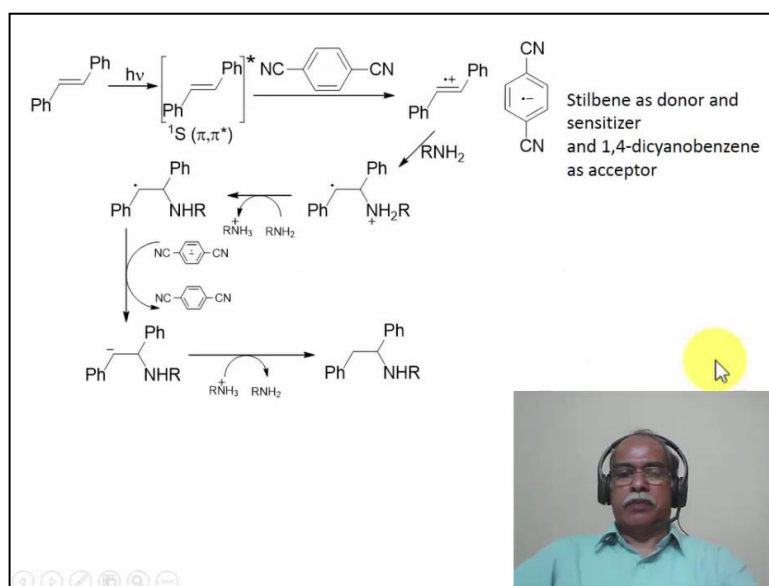
Now, Intramolecular Photoinduced Electron-Transfer process, from the Amine, to the excited state Stilbene, is what is represented here. Excitation, corresponds to the, Stilbene wavelength. So, after the excitation, to the corresponding singlet excited state, Electron-Transfer takes place, from the Nitrogen, to the Stilbene double bond. So, the Cation radical of the Amine, is produced. Anion radical of Stilbene, is produced. The Proton is transferred, onto the center here, producing the Benzyl radical, and the Amine-Nitrogen radical.

This, losses a Hydrogen, to produce the Imine. In other words, 1-Hydrogen can be transferred from here, to this position here, resulting in the formation of a saturated system. In other words, you have Hydrogenated the double bond in the process, producing an Imine, as the

final product, in this particular case. Alternatively, if the chain is long enough, the molecule can undergo cyclisation, at the Diradical stage. For example.

So, this is a 1,7-Diradical, undergoing a cyclisation process, to produce the corresponding 7-Membered Heterocyclic ring system, in this particular case. So, these are examples of Intramolecular Electron-Transfer, from the Amine, to the Stilbene, producing the Cation radical pair, within the same molecule, followed by Thermal Chemical reactions taking place, to produce the products, that are shown, in this scheme.

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Now, there is another mechanism, that can operate. If the Stilbene is excited, for example, in the presence of a Dicyanobenzene, as an Acceptor. Then, the Electron-Transfer process will be, between the Stilbene, and Dicyanobenzene, as the Acceptor, in this particular case. In other words, Stilbene is Donor, as well as the sensitizer, here. 1,4-Dicyanobenzene, is the Acceptor here. So, the excitation process takes place, to give the Stilbene excited state, the S1 state of this Stilbene.

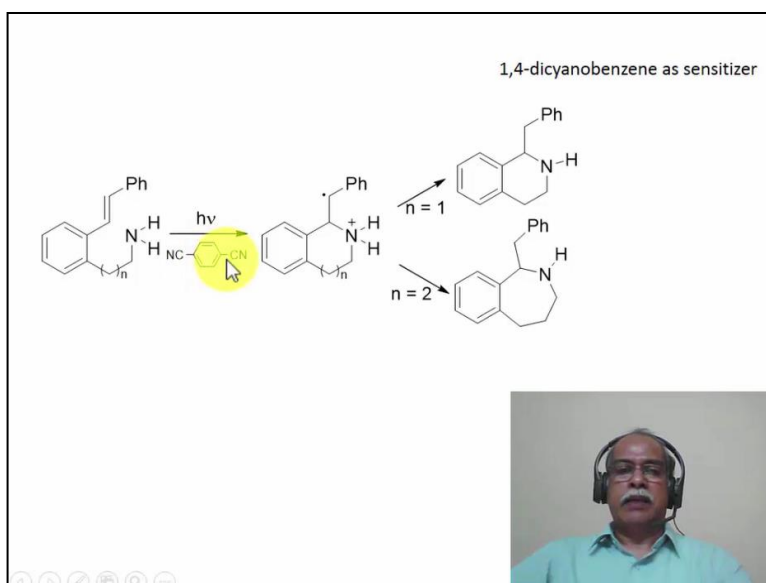
From the S1 state of the Stilbene, it undergoes now, an Electron-Transfer. The Stilbene, acts as a Donor now, donating an electron to the Dicyanobenzene process. In the process, produces a Stilbene Cation radical, and the Dicyanoanthracene Anion radical. Then, the Amine is nucleophile, now. This is electron deficient species, because it is a Cation radical, whereas this is an electron rich species.

So, essentially, nucleophilic attack the double bond takes place, to produce the corresponding Cation radical, followed by a deprotonation process is taking place, to produce the radical. This radical, now undergoes an Electron-Transfer process, from the Anion radical of Dicyanobenzene, an electron is transferred here, to produce the anion here, regenerating the

Dicyanobenzene as the starting material, is reproduced, here. This is Protonated by the Amine, to the corresponding Hydrocarbon, which is this particular Hydrocarbon.

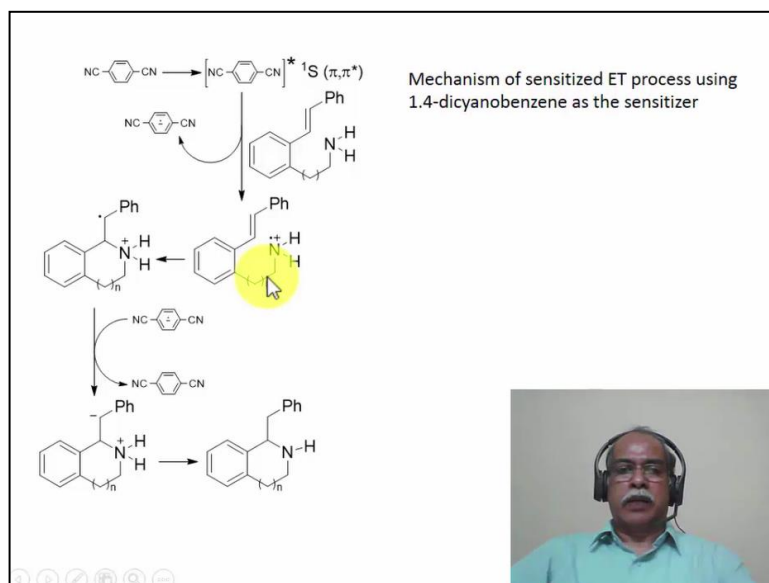
So, overall, the Amine is actually added across the Carbon-Carbon double bond. But, the mechanism is entirely different, from the earlier mechanism. The earlier mechanism, the Stilbene acted as an Acceptor, Amine acted as a Donor. In this particular case, because of the Redox potential, which is favorable for this electron transfer. The Stilbene acts as a Donor, and the Dicyanobenzene acts as the Acceptor. So, this is one way of, describing it. In this reaction, the Dicyanobenzene itself, can be used as a sensitizer, for example.

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In other words, this is photolyzed. Initially, the wavelength corresponds to the photolysis of the dicyanobenzene, which accepts an electron from the amine, for example, to produce the corresponding cation radical species. That mechanism is explained, in this particular case.

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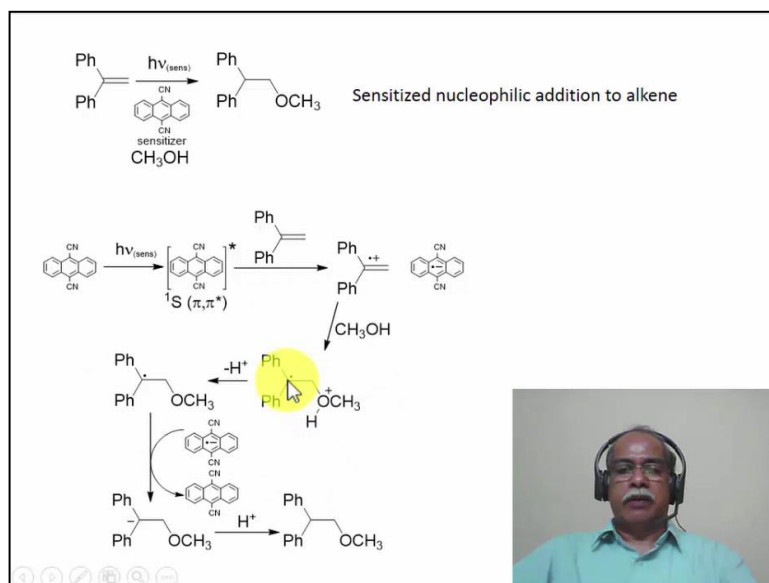


The Dicyanobenzene is excited, corresponding wavelength, is used to excite, specifically this molecule, to produce the excited state, which is a singlet excited state of the Dicyanobenzene. Dicyanobenzene, accepts an electron from the Amine, to produce the Amine Cation radical, and producing the Anion radical of Dicyanobenzene. The Amine Cation radical, is electron deficient, whereas Stilbene is electron rich. So, cyclisation can produce the Benzyl radical, and the corresponding ammonium salt, is what is produced.

Return Electron-Transfer, from the Dicyanobenzene Anion radical, to this radical, produces the Carbanion center, Benzylic carbanion. Then, the Proton transfer, essentially produces the molecule, that is shown here. So, the production of these two molecules, based on the Amine cyclisation, can be explained, on the basis of the Electron-Transfer, from the Amine to the Dicyanobenzene, which is the excited state sensitizer, in this particular case.

The sensitizer is always regenerated, in the catalytic cycle, if you look at this. For example, in this case also, the sensitizer is this, this is regenerated. This is also sensitizer, is regenerated, during the course of the return Electron-Transfer process. The Cation radical, can also be trapped by a nucleophile, such as alcohol.

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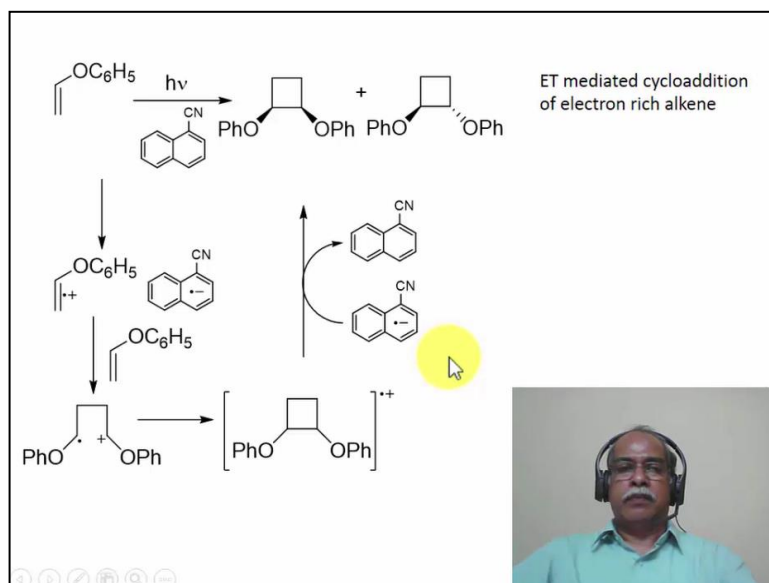


In this case, Methanol is used as a solvent, as well as alcohol trapping agent. So, essentially, the Methanol acts across the Carbon-Carbon double bond, in an Anti-Markovnikov pathway, for example, to produce the corresponding Methyl Ether of the, Diphenylethyl Methyl Ether, is what is produced, by the addition of Methanol, across the Carbon-Carbon double bond. Mechanism is simple. Dicyanoanthracene is excited, to the higher excited state.

The Diphenylethene, is oxidized by the excited state Anthracene, to produce the corresponding Anion radical of the Dicyanoanthracene, and the Cation radical of the Diphenylethene, which is trapped by Methanol, which is a solvent here, to produce this Cation radical. Deprotonation, gives the radical. Return-Electron-Transfer, from the Anion radical, to this radical, produces the anion itself, which is quenched by a Proton, to give the corresponding final molecule, that is shown here.

So, simplistic way of explaining is, shown here, in the form of a mechanistic detail, of this particular reaction. This is an example of a, Photo cycloaddition process.

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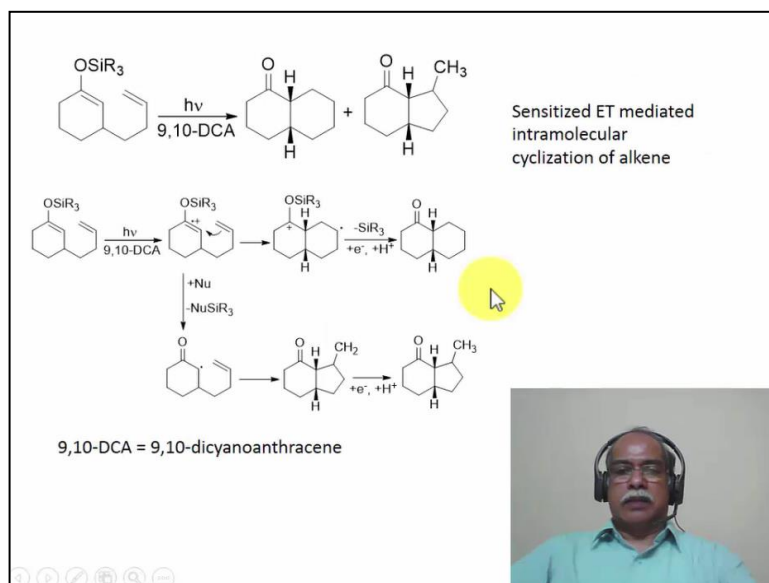


When, Phenyl Vinyl Ether is taken, and photolyzed, in the presence of Cyanonaphthalene, Cyanonaphthalene is the one, that is absorbing the energy of the photon. So, the excited state process, essentially corresponds to the Cyanoethylene. In the process, it produces the 2+2-Dimer of the Phenyl Vinyl Ether, the Cis isomer, as well as the Trans isomer. How does this reaction takes place?

Excited state Cyanonaphthalene, is quenched by the Phenyl Vinyl Ether, producing the corresponding Cation radical, and the Anion radical of Cyanonaphthalene. It reacts with, another molecule of the Phenyl Vinyl Ether, because this is electron rich process. The Carbon-Carbon bond formation takes place, producing the Oxy, the Cation radical, which is the [1,4]-Center Cation radical. This is, stabilized by the Oxygen lone pair, here. And, this is stabilized again, by the Oxygen lone pair.

This is a stable Cation radical. It essentially forms a, Cyclobutane derivative, in the form of a Cis isomer, as well as the Trans isomer. This Cation radical, has to accept an electron, from the Anion radical of Cyanobenzene. This is like a Back-Electron-Transfer, after the Chemical reaction is over, producing the product, and the sensitizer is regenerated, in the process of Back-Electron-Transfer, in this particular instance. Here is an Intramolecular version, of the cyclisation of Alkene.

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This Enol Ether, is electron rich in nature. Dicyanoanthracene, is most of the Cyano Aromatic compounds, are used as sensitizers, in many of the Photoinduced Electron-Transfer process. Because, they have good characteristic features, as far as the Redox potential, and the excited state energies, are concerned. That is a reason, Dicyanoanthracene, Dicyanonaphthalene, Dicyanobenzene, Tetracyano Naphthalene, and all those things, are used as sensitizers.

So, the cyclisation, essentially ring closes this Carbon-Carbon bond here, producing these two Ketones. The way, to explain the formation of the two Ketones, the mechanism is, what is given here. Dicyanoanthracene is excited, and it transfers an electron to the Dicyanoanthracene, producing the Anion radical of Dicyanoanthracene, and the Cation radical of the Enol Ether. In the presence of a, nucleophile like a solvent, Methanol, or something, the Trimethylsilyl group can be removed, to generate the corresponding radical.

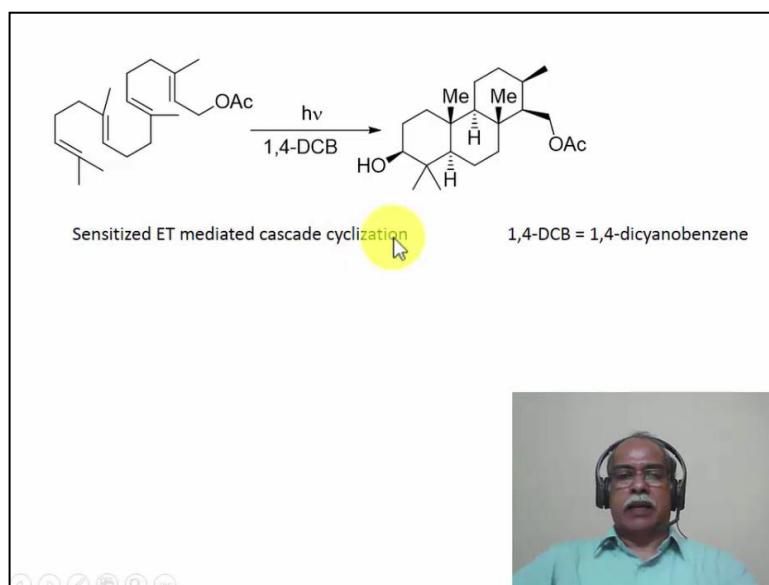
This radical, can undergo a 5-Exoteric cyclisation, to produce the corresponding CH₂ radical, for example. The CH₂ radical, is now accepting an electron from the reduced Dicyanoanthracene, to give the corresponding anion, which is Protonated, to give this particular Methyl group, here. Alternatively, the cyclisation can initially take place, to give this Cation radical.

Then, the loss of the Trimethylsilyl group as a cation, for example, produces the corresponding Diradical species, which is accepting an electron, from the Anion radical of Dicyanoanthracene, to produce the 6-Membered cyclized product. So, this is a direct Olefin ring closing reaction. This is a radical addition, to a double bond, 5-Exo radical addition to the double bond. This is a radical center. There should be a dot, on the CH₂, here.

This is the dot, has merged here. This should be, on the CH₂ here, to show that, this is a radical center. That radical center, is reduced by an electron, obtained from the

Dicyanoanthracene Anion radical, followed by Protonation, to give the corresponding Methyl species, in this particular instance. This is a fairly nice example, to show that, this kind of a Lewis acid mediated Cascade cyclisation, can also be triggered by, Electron-Transfer mechanism.

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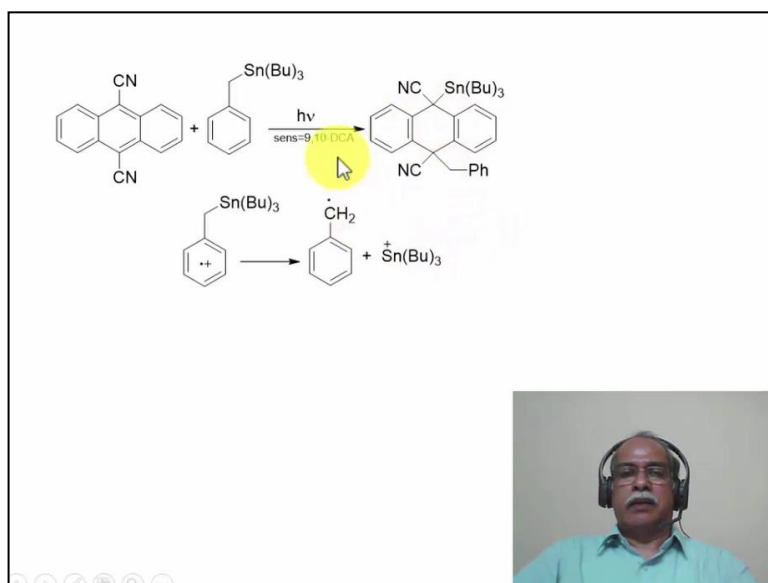


Sensitization is done by, 1,4-Dicyanobenzene. That is a sensitizer. In other words, this molecule, will undergo oxidation, reduce the 1,4-Dicyanobenzene, to the corresponding Anion radical. The Cation radical, undergoes rapid cyclisation, which is a Cascade cyclisation, to produce a steroidal kind of a system. Finally, the cation is trapped by water, to give the corresponding hydroxy species, at this particular junction.

In other words, you generate a Cation radical here, which will undergo cyclisation, essentially to produce a radical here, and a cation here. The cation is trapped by water, to produce the OH here. So, you can see, this, one Carbon-Carbon bond, another Carbon-Carbon bond, this is, one more Carbon-Carbon Bond. Three Carbon-Carbon bonds are produced, during the course of the Cascade cyclisation, from this kind of a species.

This can be cyclized, under Lewis acid conditions, under Protonation conditions also. This is a demonstration of, Photoinduced Electron-Transfer mediated, Cascade cyclisation, which is also possible, in this particular instance. Here is an example of a Cation radical fragmenting, and undergoing an addition.

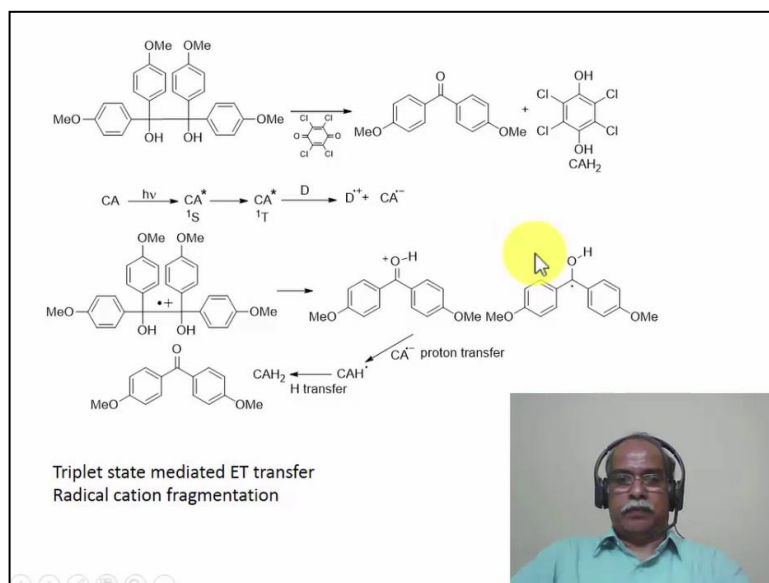
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Dicyanoanthracene, is the sensitizer. When, it is excited, the Tributyl Benzyl Tin undergoes Electron-Transfer reaction, gives an electron to the Dicyanoanthracene, to produce Anion radical, and Cation radical, of the Stannine. The Cation radical of Stannine, has a very weak Carbon Tin bond. So, it cleaves, essentially to give the Tin cation, and the Benzyl radical. The Tin cation, and the Benzyl radical, adds across the 9,10-Positions of Anthracene Anion radical, to produce this, as a final product.

So, you can see here, the fragmentation, followed by addition across 9,10-Positions, essentially leads to the formation of the product. This is a sterically hindered molecule. So, this Carbon-Carbon bond is a weak bond, which can be cleaved, under the Cation radical condition.

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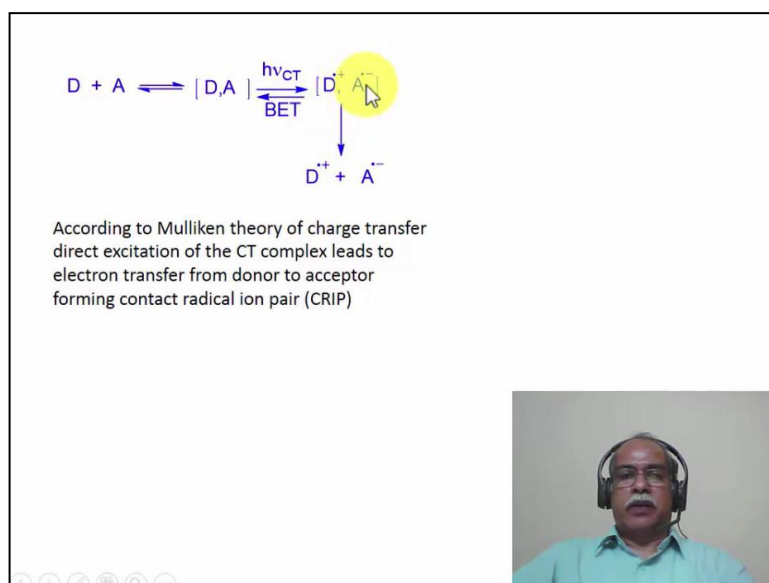
Here is an example. A triplet state mediated electron-transfer, coming from a quinone excited state, is what is demonstrated. Chloranil, is abbreviated as CA. The wavelength, that is used, corresponds to the excitation of Chloranil. Chloranil is excited, to the corresponding, first excited state. It has a, very good intersystem crossing efficiency, close to 1. So, the Triplet excited state, is formed. The Triplet excited state Chloranil, is a strong oxidizing agent.

It oxidizes the Donor, to the Cation radical. In the process, it produces the Anion radical, of itself. The Cation radical, that is produced, corresponds to this Donor. And, this bond becomes extremely weak, and it fragments, to give the Protonated Dimethoxy Phenyl Ketone, and the corresponding radical. Because, when the homolysis takes place, across this Carbon-Carbon bond, the charge resides on one Carbon, and the radical center resides on the other Carbon.

Now, Proton transfer from this, to the Anion radical of Chloranil, produces the Semi-Quinone radical. The Semi-Quinone radical, accepts another Hydrogen atom, from this particular species here, to produce the reduced compound of Chloranil, which is this particular compound, over here. And, in the process, it produces two molecules of the Para-Methoxyphenyl Ketone, as the final product.

So, this is an example of a Cation radical, fragmenting. The pinnacle, is fragmenting to the corresponding Benzhydryl radical, and Benz Protonated Ketone, which is a final product. Deprotonation, essentially produces the final product as the Ketone, in this particular case. Now, let us go back to the, Charge-Transfer excitation.

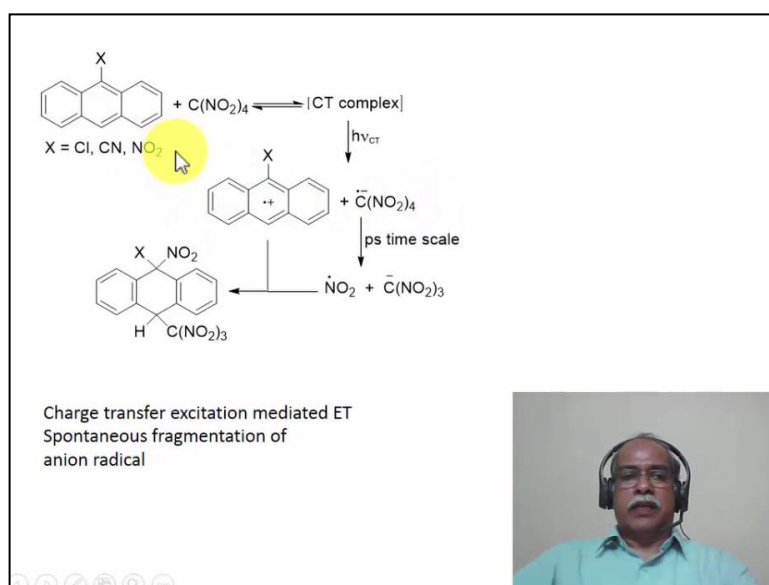
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According to, Mulliken's theory of charge transfer, direct excitation of the ground state complex, should lead to the Electron-Transfer process. And, this has been proven by, Spectroscopic methods, by looking at this compound, Cation radical, Anion radical pair, using Ultrafast Picoseconds Spectroscopy, for example. And, productive chemistry, can also be visualized.

If, the Donor and Acceptor anion radicals are not stable, if they undergo further Chemical reaction, then one can see the Chemical reactions also. The classical example of a, Chemical reaction of a Charge-Transfer complex, is the complex formed, between substituted Anthracene, and Tetranitromethane.

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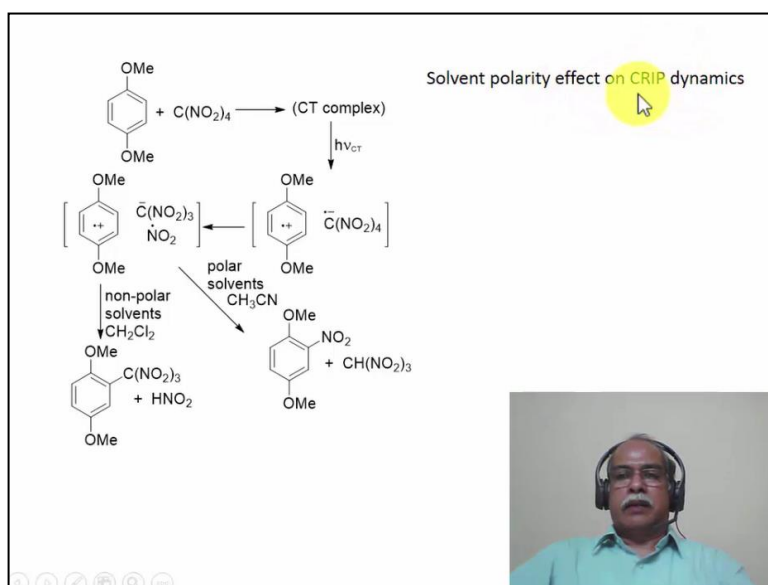
Tetranitromethane, is almost a colorless liquid. Substituted Naphthalene's are, Pale Yellow colored compounds. When, the Tetranitromethane is mixed, with the Anthracene, Deep Red, and Bright Orange colors, of the Charge-Transfer complexes, are formed. So, reversible formation of the Charge-Transfer complex, is what is implied, by this equation.

Now, if the wavelength, corresponding to the bright colors of the Charge-Transfer complex, is used for the Photochemistry, Electron-Transfer takes place, from the Anthracene, to the Tetranitromethane, which is a highly electron deficient compound, for example. It produces, the Cation radical of Anthracene, and the Anion radical of Tetranitromethane. Nobody has seen, the Anion radical of the Tetranitromethane, even using, fast timescales Spectroscopy.

Even, in the Picosecond time scale, it is not visible, by spectroscopically. It, spontaneously decomposes, to give the Trinitromethide anion, and the NO₂ radical. Now, the Radical-Radical combination at this junction, essentially produces the Benzylic cation, the corresponding Wheeled intermediate kind of a cation. The cation, is quenched by the anion. In other words, radical anion, both are added, across the 9,10-Positions of the Anthracene, to produce the corresponding product, that is shown here.

So, this is an example of a, Charge-Transfer mediated, spontaneous fragmentation of an Anion radical, followed by recombination of the radical, and the anion, that is produced by the Cation radical, to produce the product, which are stable products. The crystal structure of, some of these compounds, are known. So, it conforms, the formation of this kind of products. Another beautiful example of the, polarity of the solvent, that plays a major role in the, contact radical Ion-Pair dynamics, is illustrated, in this particular slide.

(Refer Slide Time: 42:24)



This is a Charge-Transfer complex, between an Electron-Donor, which is 1,4-Dimethoxy Benzene. The Charge-Transfer excitation, produces the 1,4-Dimethoxy Benzene Cation radical, and the Anion radical of Tetranitromethane, which fragments, to give the Trinitromethide, and NO₂. Now, we have a Cation radical, Anion radical, and a radical. Whether, the cation and the anion will combine, or the radical cation and the radical will combine, will depend upon the Solvent-Polarity.

In, solvents of low polarity, like Dichloromethane, Hexane, and so on, the Ion-Pair, Coulombic interaction is very high. So, the Ion-Pair collapses, to give the corresponding Trinitromethide substituted molecule, and HNO₂ is eliminated, in the process. On the other hand, in highly Polar solvents, where the ions are stabilized, it is a radical recombination, that takes place, resulting in the formation of the Nitro compound, and Trinitromethane, as the byproduct, formed in this case.

So, by choosing the solvent properly, one can either promote a Cation-Anion reaction, or Radical-Radical reaction, which is illustrated beautifully, using this particular example. This is an example of an, Electron-Transfer mediated, Photo Oxygenation reaction.

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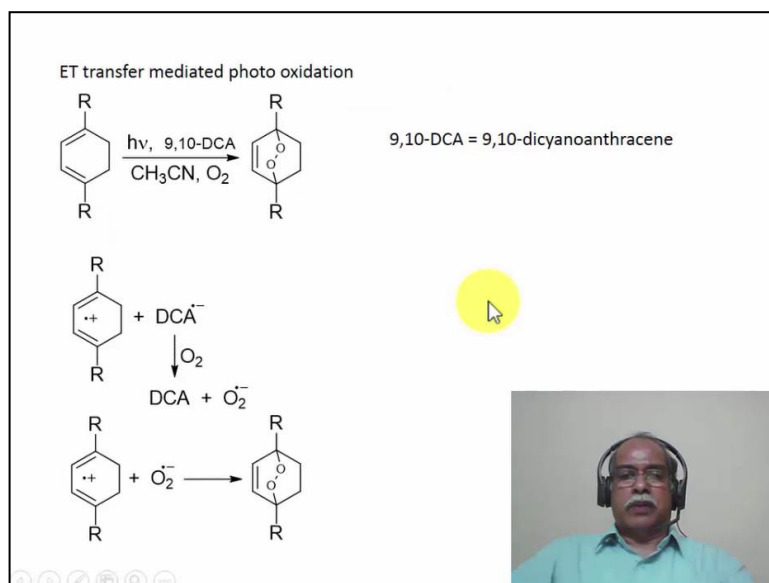
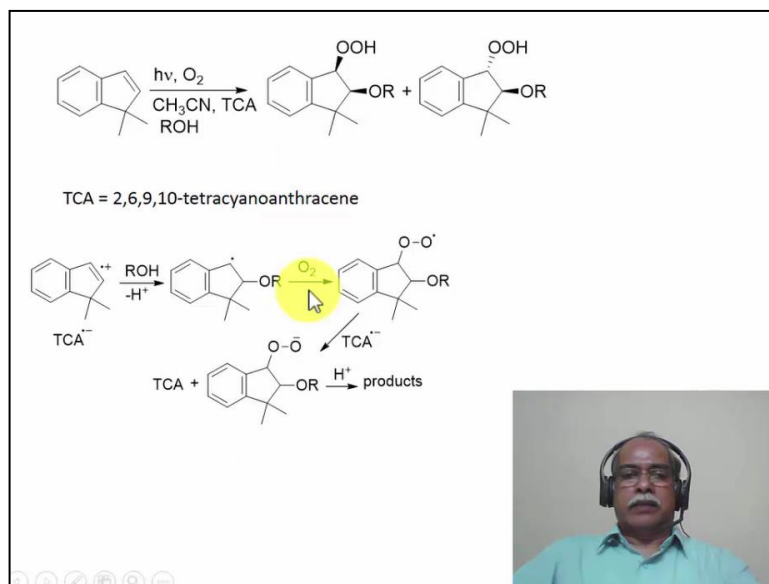


Photo Oxygenation can be carried out, in the presence of Oxygen, and a sensitizer. Here, 9,10-Anthracene, is acting as a sensitizer. The 9,10-Dicyanoanthracene, is the Acceptor. And, this Diene, is the Donor. Photo excitation of 9,10-Dicyanoanthracene, in the presence of this Diene, essentially results in the Electron-Transfer from the Diene, to produce the Cation radical, and the Anion radical, of Dicyanoanthracene.

Dicyanoanthracene Anion radical, has the right potential, to reduce Oxygen, to the corresponding Oxygen Anion radical, regenerating the sensitizer. Now, the Oxygen Anion

radical, and the Cation radical of the Diene, undergoes Deals-Alder kind of a reaction, to produce the Endoperoxide, which is a final product, in this particular case. This is a nice example of, how Oxygen can be involved, in the Electron-Transfer process, giving the Endoperoxide as the final product, in this particular case.

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Now, when Tetracyanoanthracene is used as a sensitizer, a totally a different mechanism operates. Here, Tetracyanoanthracene Anion radical, and the Cation radical of this Dimethylindene, is formed. However, the Tetracyanoanthracene Anion radical, cannot reduce the Oxygen, to the corresponding Oxygen Anion radical. For example, the Dicyanoanthracene, can have the right potential, to the reduction of Oxygen, to Oxygen anion radical. However, the Tetracyanoanthracene Anion radical, cannot reduce the Oxygen, to the Oxygen anion radical.

So, the Cation radical is trapped by Methanol, to give the product, that are shown here. The mechanism, is shown here. Initially, Tetracyanoanthracene Anion radical, and the Cation radical of Indene is formed. Indene Cation radical, is trapped by Methanol, as a nucleophile, to give the corresponding Ether, in the form of a radical.

Now, the radical is trapped by Oxygen. Remember, Oxygen in the ground state, is a Triplet Oxygen, which is a Diradical state. So, that is trapped, in the form of Peroxy radical, that is given. The Peroxy radical, is now undergoing an Electron-Transfer, from the Tetracyanoanthracene anion, to produce the corresponding Oxy anion, which is Protonated, to give this two product, in the form of Cis and Trans mixture of the product, that are shown here, in this case.

So, what we have seen, in this Module, is the Basic Elementary Concept of Photoinduced Electron-Transfer. The Energetics, that are involved in the Photoinduced Electron-Transfer. How a molecule, can be a better Donor, as well as a better Acceptor, in its electronically excited state, is illustrated. Then, the three Mechanisms of Electron-Transfer namely, Donor excited Electron-Transfer, Acceptor excited Electron-Transfer, finally, Charged-Transfer-excited Electron-Transfer.

The examples are given. Several examples of, how Cation radical can fragment, to beat the Back-Electron-Transfer process, as well as the Anion radical fragmentation, beating the Back-Electron-Transfer process, is shown here. Several examples of, Electron-Transfer mediated Chemical reactions, are also shown, in this particular module. It is a very important topic, because, Photoinduced Electron-Transfer, is the primary process, that takes place in the Photosynthesis, and Solar Energy conversion, and so on, so forth.

So, understanding the Basic Concepts of Photoinduced Electron-Transfer, is extremely important. And, that is what, we have done, in this particular module. Thank you, very much, for your kind attention.