Rate Processes

Prof. M. Halder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture No. # 23
Magneto Kinetics

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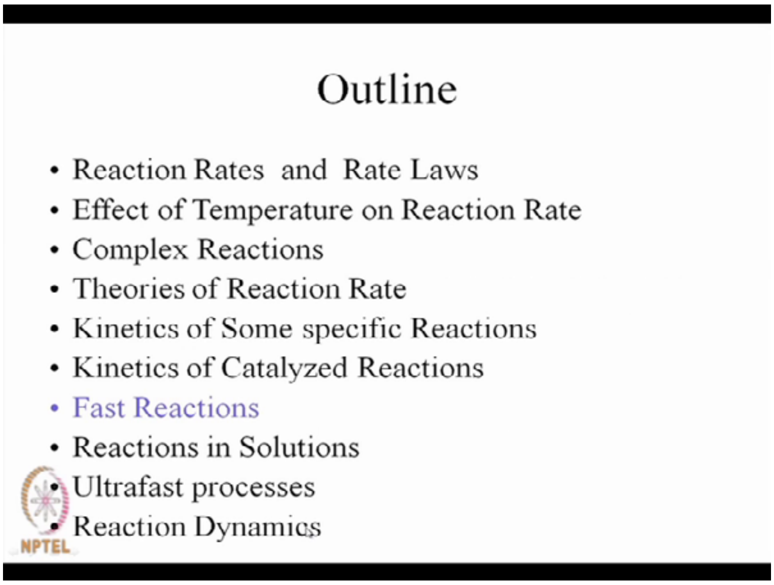

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

Hi, good morning everybody. So, today I will talk on, I mean, I will continue to talk on this fast reactions and in my last lecture I have talked about this flash photolysis. So, flash photolysis is a technique by which we can follow, you know, fast chemical reaction. It is one of the, one of the techniques by which one can follow fast kinetics. So, in that case, a modern version of flash photolysis, which is known as laser flash photolysis, so in that case, laser is used instead of flash lamp because lasers can deliver, you know, more intensity compared to flash lamp or maybe ordinary, like these lamps. So, that is why, flash photolysis is now, you know, replaced by, in most of the cases flash photolysis is replaced by laser flash photolysis and in short it is, it is LFP.

Now, using this technique, you know, one can study fast kinetics, as I gave you example of photoreaction of benzophenone. So, when benzophenone gets excited with laser of, say frequency 355, I mean, wavelength 355 nanometer…

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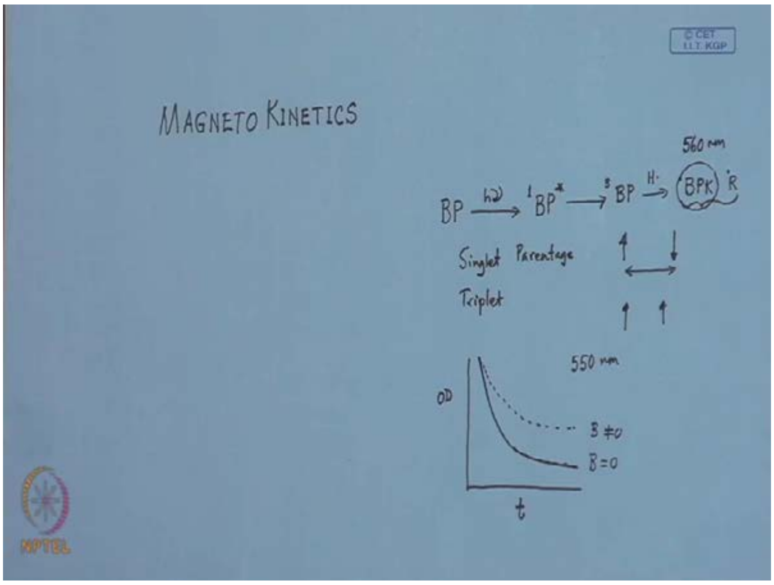

So, BP h nu BP star photo excited benzophenone. This photo excited benzophenone, then it is singlet one, then it will move onto triplet. Now, this triplet benzophenone abstracts a hydrogen atom from another molecule producing benzophenone ketyl, so H dot BP ketyl radical. So, ketyl radical plus another radical, which is coming out of the, out of the other part, which is supplying this H dot, so thereby, it is generating a radical, pair radical; pair means, a pair of radicals. Now, depending on the spin orientation, I mean orientation of spins, of this spin and this spin, this radical can have a singlet parentage or rather, it maybe singlet or maybe triplet.

So, for singlet, these two spins are like and they are located on different parts, I mean, on one is on BPK, another is on R and there is a finite, you know, separation between them. So, what will happen, that when they may form a bond, when these two, these two spins come to a bonding distance, they will tend to form a bond. Now, so therefore, this is a singlet one and triplet one can have like this, but it will have, it is a three-fold degenerate.

So, I will come to, that how it is three-fold degenerate. Now, what is happening, that if you do the experiment, experiment, that is flash photolysis, that is, you shine your sample, maybe benzophenone, which is micellized, I mean micellized within h, within SDS, sodium dodecyl sulfate micelles. So, when it is micellized and then, if you shine that micellized benzophenone with say, 355 nanometer radiation, then this will happen and therefore, a radical pair is generated. So, you know, this spins are electrons, are electron spin, because of spin they are paramagnetic. So, the substance, that is, the solution will have some magnetic behavior. So, in presence of an external magnetic field we may expect something.

What is that? That if you do photolysis in presence of an external field, say, you know, by means of a simple bar magnet if you shine your sample in presence of, say this is your bar magnet, you just take your bar magnet close to the sample compartment or maybe close to the quvect and then, you shine the radiation, then some differences may be expected.

So, in my last lecture, I was giving you the idea of the signal that say, this is the, say this is the decay profile, decay profile, that is, as a function of time. Of course, this time scale is of the order of several nanosecond, maybe even 2 microseconds and this is your OD or maybe delta OD as well. So, what is going on, that if you monitor your signal at, say 550 nanometer, then you will be getting a decay of this sort. So, in presence of external magnetic field, B external is equal to 0, now you increase your magnetic field. So, if there is no effect, then you, you, if there is an effect of your external magnetic field, then you may expect, that your decay profile will merge; new decay profile will merge with old one. If there is no such, you know, radical pair formation and there, you know, dynamic behavior is not affected by the term dynamic behavior, that how they, their spin orientation, I mean overall spin is, you know, evolving with time. So, dynamic behavior means, maybe it started with a singlet radical pair case and ultimately, it is converted to a triplet one or maybe vice versa.

So, that, that is, you know, with time the description, that is, the description of singlet state to triplet state or triplet state to singlet state, that may happen. So, what, what has been found is that, that in presence of an external magnetic field, that is, B not equal to 0, that is, you are applying some external magnetic field, maybe static magnetic field and it is found, that it is like this. So, the decay kinetics, decay of your, your, your, this BPK because you are monitoring your ketyl at say, say 316, 560 nanometer or 550 nanometer, so decay kinetics is found to get altered.

So, why this is happening? Why the, I mean, in presence of an external magnetic field, something is happening, so that this decay is getting affected. So, magneto kinetics is a branch of chemistry, which is known as spin chemistry, where we deal with speeds; here we deal with electron spins.

So, in presence of an external magnetic field, how they spin? I mean, spin of an electron, its projection is, you know, getting affected in presence of an external magnetic field. How this is affected and how this is going to alter the kinetics of the process? Kinetics of the process means, you know, maybe it is a back hydrogen transfer process, maybe back electron transfer process or maybe or maybe other kind of recombination. By the term recombination, that you have say 2 radicals and they will recombine to form a bond, that is called the recombination; so, so recombination.

So, how this is going to, I mean, this process is going to be affected in presence of an external magnetic field, that we are trying to, trying to focus and that is the, that is the, you know, you know, main thing in the, in magneto kinetics. That is, effect of external magnetic field on kinetics, on the dynamic behavior of radical pair and broadly speaking, here we are looking into dynamic behavior of recombination of radical pair.

So, we are just, we just try to, try to find out the answer. I mean try to, try to give you, I will just try to give you an idea, an overview of the process, what is going on with this, with this spins. Once these radicals are generated, radicals may be generated by homolytic cleavage of bond or maybe excited state atom transfer, maybe excited state electron transfer; there are various ways by which, you know, radicals and radical pairs may be, may be generated.

So, it is a, it is a photochemical generation of radical pair, it is a photochemical means, that is, you shine your sample with photons getting excited. Then, this excited ensemble of, you know, molecules will, excited ensemble of molecules will do further reaction, maybe a cleavage of bond, homolytic, or maybe, you know atom transfer, like I, I told. Here, this hydrogen atom transfer or maybe electron transfer as well, that is the excited ensemble, may accept an electron from an electron donor or maybe excited ensemble of molecules will donate 1 electron to another acceptor, maybe it is in the, preferably it is in the ground state.

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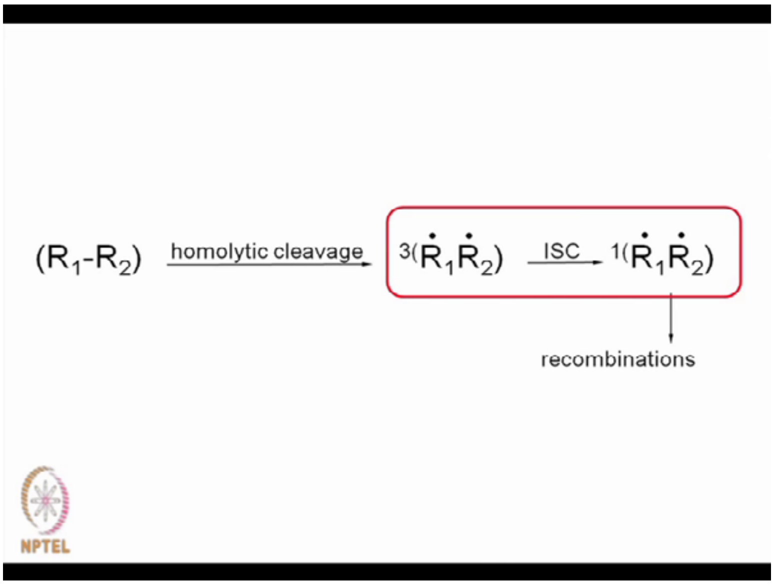

$$(R_1\text{-}R_2) \xrightarrow{\text{homolytic cleavage}} \boxed{{}^3(\dot{R}_1\dot{R}_2) \xrightarrow{\text{ISC}} {}^1(\dot{R}_1\dot{R}_2)}$$

recombinations

So, let us, let us look into, let us look into this, that is, we have got, we have got this R 1, R 2 is a homolytic cleavage, maybe producing a triplet radical pair via intersystem crossing. It may get converted to a singlet radical pair. It is a radical pair means, the radicals are, maybe, formed within a, within the same solvent cage; it may be, may be formed in a different solvent cage.

So, if it is in the same solvent cage, it is called the geminate pair and the corresponding recombination is called the geminate recombination producing your bond and making, I mean, generating the original species back or maybe, a new species formed. So, it is a homolytic cleavage, that is responsible for this formation of your triplet, maybe something else will also happen, that by homolytic cleavage, maybe, singlet radical pair is also generated, which will undergo intersystem crossing to produce the Triplet one. So, only difference is, that singlet radical pair will have like this, this one and triplet one will have this one. But this is not the only description, it has 3 options; 3 options means, I mean, it is a triply degenerate.

So, therefore, in absence of an external magnetic field, this triplet degenerate states are, are having the same energy. The moment you, you apply some external field, this degeneracy is lifted and thereby affecting, and thereby affecting, you know, the intersystem crossing, crossing process. So, here, intersystem crossing is, is happening in a, in a, in a little bit different way, let us see.

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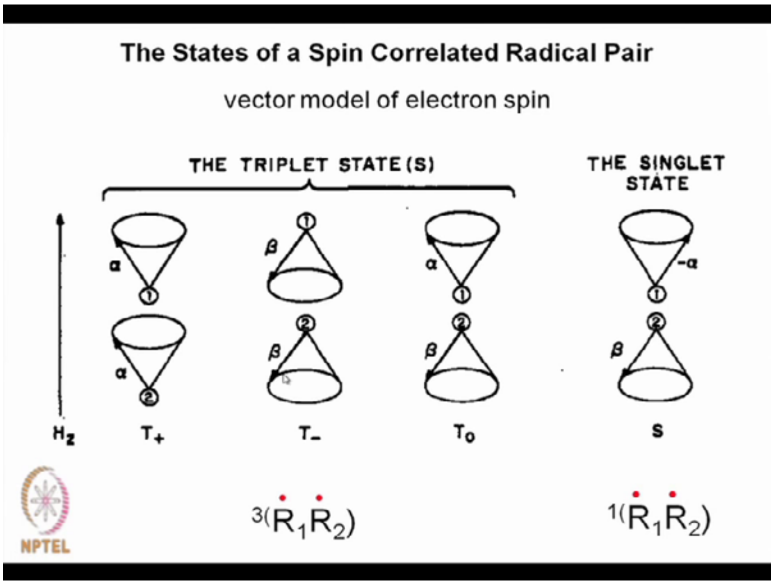

The States of a Spin Correlated Radical Pair

vector model of electron spin

${}^3(\dot{R}_1\dot{R}_2)$

${}^1(\dot{R}_1\dot{R}_2)$

So, let us, let us look into the, into the radical pairs, spin correlated radical pairs. There may be uncorrelated radical pairs, we are not interested into that. We are interested into those, those radical pairs, which are, you know, having maintaining the correlation. Now, triplet state has 3, 3 options. Here, one is this spin 1, this is spin 2 and it is shown, that is the tip of the vector is making a cone, it is just like a funnel, this is another funnel. So, see, both are, both are up; both are up means, its zee projection, projection in the z-axis, all these, these, for these two are plus half.

So, therefore, it is alpha spin; so, alpha, alpha. So, one spin function is alpha, another spin function is alpha. So, combine, for triplet 1 alpha, alpha is 1, one description; in another case, it is beta, beta; see, both are down. So, z-projection is minus half, minus half. Here, it is a linear combination of alpha and beta; it is a linear combination of alpha and beta, alpha 1 beta 2, of course with proper normalization constant. So, so the thing is, that this is a linear combination, this is another linear combination, this is a linear combination alpha plus beta, this is beta minus alpha, why? Because this is minus, I mean, in, in, in the reverse sense.

So, you see, that, that this is the singlet state that is the only description; it is a true spin opposed, you see that. If you see, if you see, then it is truly opposed in the sense, that these two vectors are exactly opposed to each other like this, like this, like this. This is your z-axis, this is your z-axis; this is your z-axis. So, they are, these two are exactly opposed. But what happens, in case of your, of your triplet, you see, this is your z-axis and this is plus half, this is minus half, but it has got a resultant in this direction and the projection of this resultant on this axis is 0. So, their resultant is not truly 0, but their projection of the resultant on this zee-axis is 0, that is why it is it is called, you know, T 0. So, this is T 0, this is T minus, that is both beta and this is T plus both, alpha and this is, one is beta, another is alpha of course, with, with you know, they are exactly 180 degree.

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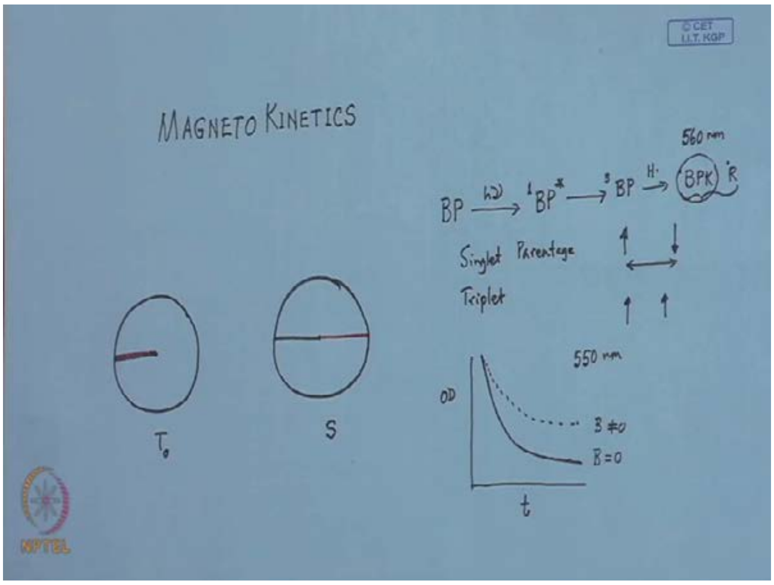
MAGNETO KINETICS

$$BP \xrightarrow{h\nu} {}^1BP^* \longrightarrow {}^3BP \xrightarrow{H\cdot} \boxed{BPK^\cdot}\ {}^\cdot R$$

So, if you view from the top, then for your T plus… So, you see, that for your, for your T plus, you are, you are viewing from the top, this is for your, say S, this is for T, so T 0. So, then it is the other one, other vector here, it is in the same direction if you view from the top; you have to view from the top. So, this is a truly, truly spin opposed, therefore it is singlet.

Now, the question is how this singlet to triplet transition is happening? Now, I guess all of you know, that molecules, in molecules when a radical, I mean a dot is created at some point of, I mean, I mean some portion of your molecule, then that dot, that dot is experiencing some internal magnetic field, some internal magnetic field and that, in presence of that internal magnetic field, you know, in absence of the magnetic field, they are oriented randomly. But the moment your external field is applied, then this spin, spins are going to, I mean, they, they start processing about that axis like this, like this. I mean, this is your axis; it is processing like this, like this it is processing. Now, this processional frequency is very much dependent on the magnetic field, it is experiencing. So, the question is, you can, you can, I mean, the phase difference here, for this one phase difference is 0.

You see red and black, both are you know having the same angle. I mean, if you, if you count this angle, then both are having the same angle and here they are, I mean, angle was there 180 degree apart. So, they are in phase, they are opposed, there phase angle is 1; if it is 0, then it is 180. Here, both of them are either 0 or 180.

So, how can you, how can you get this picture from here to here or from here to here? If they maintain a constant phase difference, then what is going to happen, that like, say this one, if they maintain a constant phase difference, they will do like this for this one, for this one they will do like this; if they maintain a constant phase difference like this, they will do like this. And in, in other case for this one, they will do like this; they will do like this.

So, what is happening, that, that suppose, by some means if you can increase the processional frequency of one of these 2 spins, then there will be dephasing, that is, maybe this red will move a little faster than this one. So, at one point of time, this red will merge on this. So, red will merge on this means, you are getting this picture; so, that means, the merged red on black is basically triplet. So, basically, you have got a transition from singlet to triplet 0 or vice versa, that, such that, that if black is moving faster than red, then you may get a picture of this and that is called a singlet. So, in this way, if you can, if you can change the relative processional frequency, then you know, then you can, you can shift from T 0 to S or S to T 0. So, so that is one way of transforming the system from, you know, from T 0 to S.

Now, how, how can you get, how can you get, you know, this from T 0 to T, T minus to T 0? So, that will require, that will require flipping; that will require flipping of this beta spin to alpha spin. That means, you need to change this, this one to this one. How can that happen? That, that if you can apply an external magnetic field, such that this external magnetic field is perpendicular to your, to your internal magnetic field or maybe, there is an, there, there is another magnetic field, which is operative in this direction. So, this is your original, original space, fixed axis, but maybe, some internal field is there or maybe, something else, that we are not concerned right now. So, so suppose, that is your, this is, this one is your additional field, so and that field is very close to your beta spin over here, so that this additional field starts the procession of this beta 1 along this axis. So, this will do like this.

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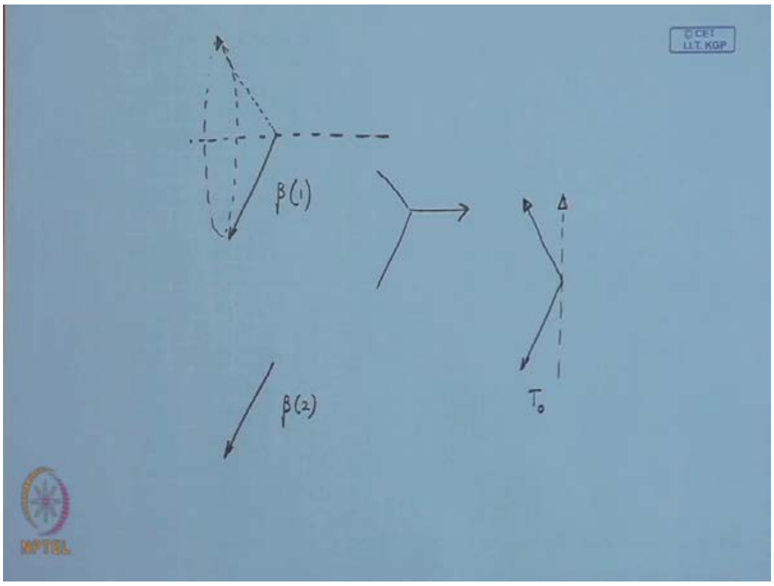

In doing so, what is happening that, let us draw another picture, in doing so, that originally it was like this, this is your beta spin, this is another beta spin. You, you are having this extra, I mean, additional magnetic field, which will start the procession. This is your beta 1, this is beta 2, so it will start procession around this axis, so that this tip of the vector is now here because of this procession.

So, ultimately, what you are getting? This plus this; so, your picture now becomes this one and that one and you try to match. This is nothing, but your, this is nothing, but your T 0. This is your external, I mean, space fixed axis. So, that means, because of this additional procession, that means, you need to, you need to change your, change the angular momentum, so that is compensated by the additional field; compensated by the by the 2nd field. So, there is a, there is a, you know, conservation has been, conservation of angular momentum has been done in this way. So, it is nothing, but a transition from T 0 to T minus or T minus to T 0. In the same way, you can have, you can have transition from, you know, T plus to T 0; T plus to T 0.

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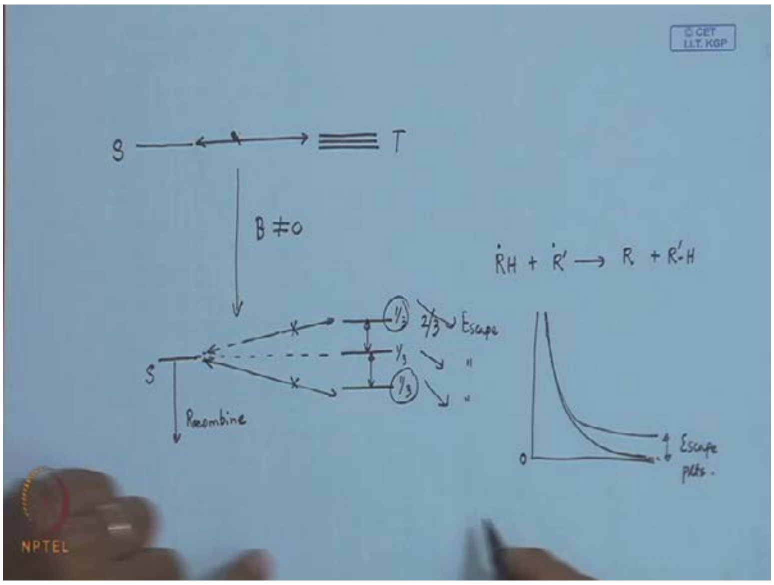

So, so, basically what is happening, that, that, so energy, energy level-wise, energy level-wise we have, say this is your singlet S and this is your T; this is your T, of course, it has got 3, 3 levels. So, in absence of any external magnetic field, there is, I mean, there is a transition between singlet and triplet.

Now, what you do, you apply your external magnetic field H or E, I mean, B is the external magnetic, B is not equal to 0. So, what is going to happen then? Then, this, this triplet becomes like this and depending on the strength of the external magnetic field, this splitting will, you know, will change with external magnetic field strength. So, now what is happening, that energetically these two are same, but these two are different. So, transition from these two is now getting reduced because, because of the energy gap, energy gap factor, because energy gap is there. So, this gap is dependent on your, this splitting is dependent on your external magnetic field.

So, two-third of the total population; so, this is one-third, this is one-third, this is one-third. So, these 2, 2, two-third of the total triplet population cannot, cannot now get converted to singlet. So, what is happening that they will not recombine; recombine means, say, say RH, say dot plus is another R dot. So, recombination means, maybe, say R prime, say R plus R dot H. So, this is your back hydrogen transfer or maybe, recombination. So, what will happen? They will not recombine; only one-third of the total triplet population may communicate with singlet and hereby go to, thereby go to singlet and recombine.

And here what they will do; when the system is in the triplet set, what they will do? They will simply escape. If the system is in triplet, they will have the least tendency to recombine, I mean, because of their spin arrangement. You see, unless they are like this, unless they are like this, I mean, these spins are like this, they will not form a bond. Therefore, whenever, whenever the system is in triplet state, they will recombine, I mean, they will separate out producing free radicals. But when they are in singlet state, they will quickly recombine to make, to form a bond. So, so that is, it is written as escape, escape.

So, it is simply cage escape or escape and here it will recombine. So, what will happen? So, when there is no external magnetic field, these triplets could have the option to move to singlet or it may escape, but since this channel is, channel producing recombination product. Therefore, you know, the recombination is expected, more recombination maybe expected because it is a very fast process. But when you apply external magnetic field, what is going on? When there is an external magnetic field, then two-third of the total population is now, you know, here one-third is here, another one-third is here. So, they are, they are energy-wise more compared to this singlet and T 0. Therefore, their option is only to escape producing cage escape products. That is, you know, radical pairs are now separated out and they will no longer recombine because they, they will now become a part of, you know, different, different, maybe cage. So, it will be very difficult for them to recombine or maybe, they will, they, they will combine, but that is not something, you know, something what is happening for your correlated radical pair.

So, those are, those are becoming uncorrelated radical pairs when they are away from bonding distance of the, say of the order of 8 to 10 angstrom. More than that, then there is no roughly, I mean, there is no, you know, interaction between them, so they will remain as free radicals. So, that is why, when you take the signal from, look into the signal from the (( )), you will be seeing, that if it is a truly 100 percent recombination, then this is your 0, I mean, 0 of y-axis. So, so this will go very close to 0 of y-axis, but if there is a fraction, that is not undergo, you know, undergo full recombination, then what is happening? That it may happen, but maybe there is some residual signal. So, this corresponds to your, corresponds to your escape products, escape products.

So, what, what experimental observation we may expect here? That in presence of external magnetic field, if it is a singlet bond radical pair, what is going to happen? Singlet bond radical pair and triplet bond radical pair will behave in opposite fashion. So, singlet bond radical pair, immediately after, you know, immediately after its birth, it will tend to recombine. But if it is a triplet bond, it will not recombine immediately after its birth; it will have to recombine by transferring from triplet state to the singlet. So, it will recombine through this. So, any hindrance in this path will reduce recombination. So, the same way will reduce recombination for triplet, but for singlet, if there is a hindrance, then we may expect more recombination because this channel is off, I mean, because of magnetic field, maybe two-third of the, of the total population, I mean, two-third, two-third of the, I mean, out of 3, 2 channels are off because of external field. Therefore, maybe one-third has the option, option to escape. So, that means, escape products will be you know, you know, reduced, when it is a singlet bond radical pair.

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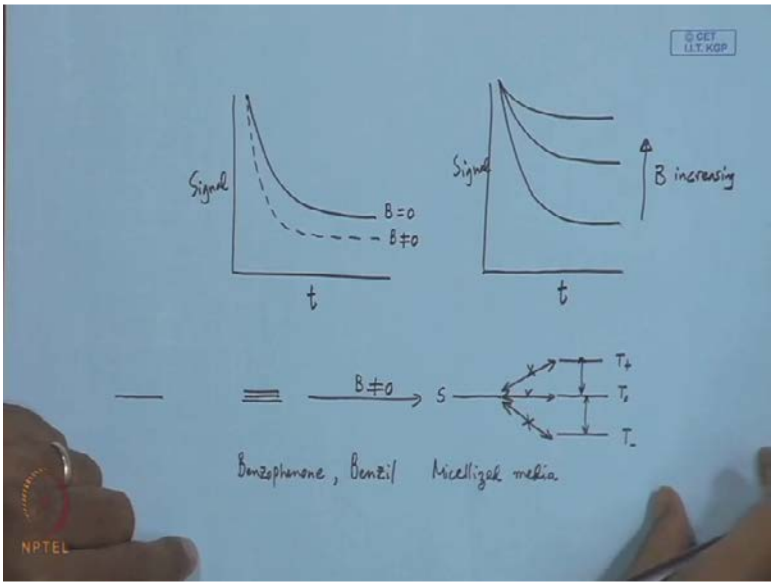

So, for singlet bond radical pair, in absence of an external magnetic field, if your profile is like this, maybe, you can expect like this in presence of B not equal to 0, B. For your triplet bond if it is like this, maybe you can expect and maybe with increasing magnetic field, it will be like this, B is increasing; B increasing. This is your signal, maybe OD or similar quantities and this is T. Reverse maybe expected, you know, for singlet bond radical pair. So, that means, you have got this energy level diagram in absence of external magnetic field, you apply B not equal to 0, then you, you have this option T 0, T plus, T minus and this is your S.

So, this channel remains open and depending on the field strength these channels are progressively blocked; these channels are progressively blocked. So, two-third of the population in the triplet state cannot, you know, recombine. That is why, for triplet bond radical pair, here you see, this escape yield is increasing because, you know, majority of your radicals, I mean two-third, about 66 percent, 66 percent cannot, you know, come to singlet state, singlet radical pair. Therefore, you know, this escape yield is increasing and this, this has been found to happen with, say benzophenone, maybe benzyl, and similar, hydrogen, for similar hydrogen abstraction reactions, benzophenone or benzyl in, in micellized medium, micellized medium.

But in other case, if you take, you know, this, if you take neat solvent, say for benzophenone, do you expect you know any magnetic field effect? The answer is, magnetic field effect is, magnetic field effect is, you know, very feebly seen or maybe sometime you cannot detect any magnetic field effect, why it is so?

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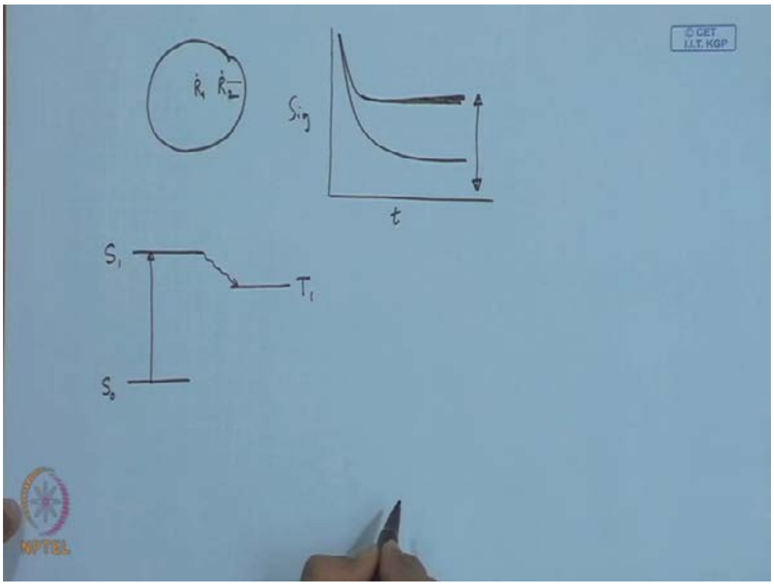

Because micelles provide, you know, say this is your micelle, micelles provide… Suppose your radical pair is generated, say R 1, R 2 generated over here. The moment it is generated, if it is a, it is a neat solvent, they have the option, maybe to come close or maybe they, these have the option to go away. So, one it, once it, once they go away, then it is very difficult for them to come back. There must be some, some boundary, which resists them to, you know, separate out; separate apart.

So, micelles, rather provide such a, an environment this micro-heterogeneous, you know, medium. It is, it is a combination, I mean, it is, it is an aggregate of surfactant molecules. So, what is going on, that the moment it is generated, they will, you know, try to go this way or maybe, come close to each other, but those, which are going this way, will, will be reflected, so reflected by this boundary. So, these micelles, it is basically, they are providing reflective boundary, so that these radical pairs will stay for sufficient time, allowing this spin evolution to take place. Of course, this micelles have, you know, opening, I mean small opening, so that the radicals can escape. That happens, but most of the radicals will, will tend to, you know, you know, will tend to remain within this micro cage, so that the spin evolution can take place.

Spin evolution can take place means, as I mentioned, that is singlet, I mean, singlet to triplet or triplet to singlet evolution and of course, it depends on the distance also, that when they are very far apart, then there is virtually no interaction. So, above 10 angstrom, there is no virtual interaction, but if it is within, within, you know, 10 angstrom, then singlet and triplet will follow different, you know, potential energy curve. So, and if a system falls, I mean if a radical pair is in the singlet state, then option is recombination; if it is in the triplet state, option is, you know, the cage escape.

Now, how to prove, that these radicals, I mean, these radicals, for this radical pair, you know, spin chemistry, how to prove, that this micelles provide reflective boundary for the enhancement of this magneto kinetic phenomenon? Now, in one case, the, the, the, the experience is, that if you do the experiments in neat medium, then it is very difficult to see, it is very difficult see any magnetic field effect. So, magnetic field effect, if it is there at all, it becomes very feeble.

So, how to, how to look into the actual rule of your micelle? It is very simple, that if you make some mixed micelle or maybe, if you can modify the micelle, such that its reflectivity is reduced and its, you know, this openings are increased, then what is going to happen? So, that can be done by using, you know, secondary additives like dioxin or similar small molecules, that this dioxin or other, other similar molecules form mixed micelles. So, if, if, if they form mixed micelles, then micellar, I mean, escape rate is increased because the, I mean, the openings are increased.

So, escape rate is increased means, escape rate is increased means, you know, you will, you will expect more of, you know, escape product, rather than the cage product; cage product is recombination. So, your, your, your profile is in absence of, you know, this dioxin and in presence of dioxin we will be seeing, that dioxin increases this cage escape and sometime it has been found, that, that magnetic field effect is also, you know, reduced. The extent of this signal, this time magnetic field effect is reduced. So, that means, by, by formation of a mixed micelle, the cage escape rate is increased and thereby magnetic field effect is reduced. So, that is why, means for observation of your magnetic field effect it is, it is, you know, more important if you, it is more important if you can micellize your radical pair within the micelle because micelles provide reflective boundary.

So, so, it is a, it is a very interesting thing, that this singlet to triplet intersystem crossing, although in case of molecular system it is not a, that the molecular triplet. You, you must remember, that, say, suppose we have got a molecule with, say, having a (( )), that ground state is singlet, 1st excited state is also singlet and maybe, there is a triplet state T 1. So, what is happening? When you shine, it absorbs light, goes to singlet and then, from singlet it moves to triplet depending on spin orbit coupling. So, when spin orbit coupling is high, then possibility of this transition is more because of spin orbit coupling possibility is more.

So, so, what is going on? That for this transition, this type of molecular singlet-triplet transition, you do not expect any, you know, any external, you know, effect of an external magnetic field. But when it is the question of molecular, not, not the question of molecular triplet, but when it is the question of, you know, radical pair triplet or radical pair singlet. In that case, in that case, you can expect magnetic field effect. Sometime it is referred to as the molecular magnetization, that is, this molecules, I mean, radical pairs, they behave like tiny magnets. And in presence of, you know, external magnetic field, their spin orientations will change and as a result of which the relative population of one state is changing with respect to the other state, and thereby you, you see some nice observations.

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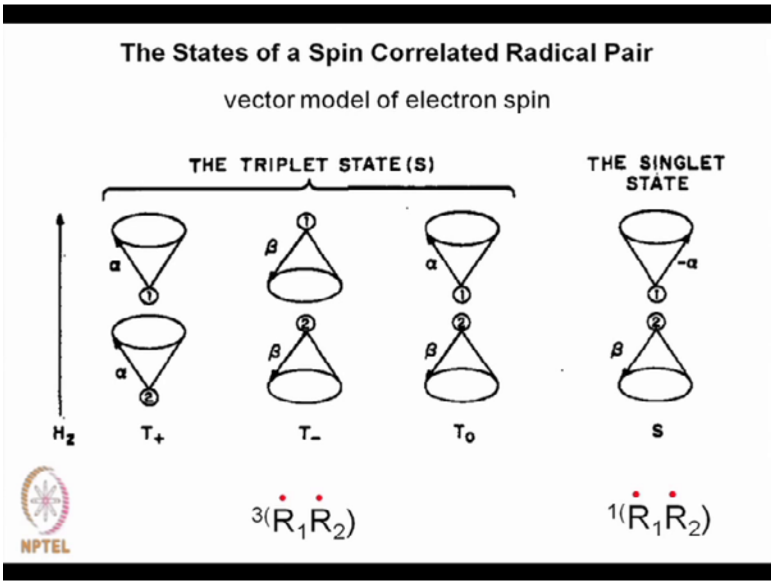

The States of a Spin Correlated Radical Pair

vector model of electron spin

$^3(\dot{R}_1\dot{R}_2)$

$^1(\dot{R}_1\dot{R}_2)$

So, referring to this vector atom model or vector model of electron spin, we have seen, that you know, say this is your, you know, 2 alpha spin up, here 2 beta spin down and this is the combination of alpha and beta. So, and transition from this whole ensemble, from here to here is possible, you know, by, you know, internal field; internal field driven, it may be possible or maybe, external field driven as well. When there is no external field, then maybe these 2 and these 3 can freely transfer from here to here, but how much it will transfer, that depends on, on, you know, how fast, you know, this state is transferred to this state. Sometime it may be very slow process, that singlet to triplet transition is slow and even in the absence of an external field. But, when field is applied, that maybe, that, that transition from singlet to triplet may get affected.

So, so importantly, so what do we do? We get out of it, that, that spin chemistry is a new branch of chemistry, where we deal with, where we deal with spins when it is the question of spin. And when it is the question of radical pair mechanism, it is this mechanism is called the radical pair mechanism. It is a well established mechanism, that radical pairs will form from either, you know, a singlet or maybe a triplet or sometime it is interesting to note, that maybe it is a, it is a mixture of, you know, singlet and triplet; it is a strange mixture of singlet and triplet.

So, in that case, you know, the situation is further complicated, which I am not going to discuss in detail, but just I wanted to give you a flavor of what is going on in this with,

with this spins on molecular levels. So, so what is important, that you know, spin chemistry is a, is a, is a very important branch of chemistry, that, that a lot of research work, you know, I mean, maybe lot many papers are published there, which deals with, you know, effect of external magnetic field on radical pair, you know, dynamic behavior of radical pair recombination. So, by applying, you know, external magnetic field, you can in principle alter the reaction rate. Why I am talking about reaction rate? Because our main, you know, projection for this series of lectures is kinetics.

So, we have, we have, we have talked about, if various external factors, that you know, affect the kinetics of a process like, you know, temperature, maybe pressure. So, these are the, you know, temperature, pressure, you know, you know, like you increasing, temperature rate is increased, but, but external factor like, you know, ionic strength is also known to affect, you know, this ionic reaction rates, like, like these, these factors. Magnetic field is, is another factor, which I have shown to you, that it is also, it can also affect the chemical reaction. That if you, I mean, if you think of a radical reaction, suppose a reaction, which, which occurs by radical mechanism. When it occurs by radical mechanism and if, if you know similar things happen, like say, a pair of radicals, they, they maintain, you know, spin correlation.

Then, this spin correlation maybe, means for this correlated spins, if you apply external magnetic field. Then, maybe triplet manifold is degeneration between triplet manifold is, you know, lifted and thereby recombination tendency or maybe recombination tendency or maybe just escape tendency is altered. So, altered means, you expect, you know, maybe some different result, I mean different, I mean, different product or maybe, maybe amount, I mean, yield of product, yield of product is reduced maybe. So, in that respect it is a, it is a, it is an important, you know, field, it is an important field and maybe, maybe various, it has been found for various reactions like, reactions like, you know, like this hydrogen atom transfer reaction, maybe electron transfer reaction, where specially for micellized radical pairs, specially for micellized radical pairs, you know, we expect, we expect effect of an external magnetic field. So, therefore, we can, we can say, that by applying external magnetic field, not only like, you know, pressure, temperature, maybe ionic strength or maybe changing the solvent, but external factors like, like magnetic field is, you know, has been, has been shown to be very effective in, in changing the overall rate. That is what it is, what it is doing is that it alters the singlet to triplet interconversion rate, singlet-triplet radical pair, singlet-triplet interconversion rate. So, if this interconversion rate is altered and you know, that singlet state, singlet radical pair generates cage product or maybe recombination product and triplet radical product, I mean, pair will generate, you know, escape product.

So, therefore, application of magnetic field will alter the singlet and triplet population or maybe, maybe interconversion between them and thereby, overall reaction is affected. So, this, this embodies a nice, you know, demonstration, that, that magnetic field effect, although it is not, you know, you, you are applying magnetic field, field from, from a distant place, but a distant place, but, but it is, it is, it is affecting your process not for all reactions, but for reactions those are, those are via, those are via radical pairs. And for micellized radical pairs it has been found, that this effect is, you know, is magnified because micelles produce, micelles provide, you know, reflective boundary, that the radical pairs are required. That is, a round trip excursion of the radical pair is necessary for their recombination because micellar cage provides a possibility for recombination. If there is no cage, they will always escape, but when there is a boundary, these radical pairs will get reflected from the boundary and then will have the option to come close, and if they are with proper spin orientation, they will recombine.

So, you know, by the use of vector atom model, we have been able to, able to, you know, we have been able to, able to give you some idea, we tried to give you some idea of a spin chemistry, that is the chemistry going on with spins because it is, it is a more detailed description, because spins are responsible for the formation of bond or maybe, maybe cleavage of bond. So, we are in the, in the deeper, deeper side.

So, if you, if you want to know more on this spin chemistry and recent developments, you can, you can visit Nicholas J Turro’s web site. He is in the Colombia University chemistry department. So, and there, there is a popular text by Nicholas J Turro is also available in the market. You can, you can or maybe in the library you can, you can, you can go through that to get more examples, more, more, you know, you know, more, more points or maybe, recent advances, more and new results.

So, this, so this spin chemistry, description of spin chemistry, you know, is as, is as a part of, you know, application of flash photolysis because flash photolysis technique we use to study. So, flash photolysis technique means, you know, you just do flash photolysis in presence of an external magnetic field, that is what you know, what we need and generally, the time scale is nanosecond to microsecond; time scale of observation of the process, of the observation of the phenomenon. So, so, that is all about, you know, a brief, this is basically nothing but a brief introduction of spin chemistry. We are not going to, going to details of it because it is, it is, it is a broadly, it is a kinetics class. So, so this completes the, you know, fast reaction techniques and its application. So, in the, in the next lecture, we will focus onto, on to various reactions, especially that are occurring in solution phase, maybe some diffusion controlled reaction, maybe hydration factors affecting hydration, etcetera. So, till then have nice time.

Thank you.