Mechanisms in Organic Chemistry
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Lecture-05
Reaction Co-ordinate Diagrams

So welcome to the second week of this course on reaction mechanism. So just to summarize what we did the last week, so in the last week what we look that is how to actually write reaction mechanism using arrow pushing or electron pushing and we are also specifically looked at two major classes of organic reactions,

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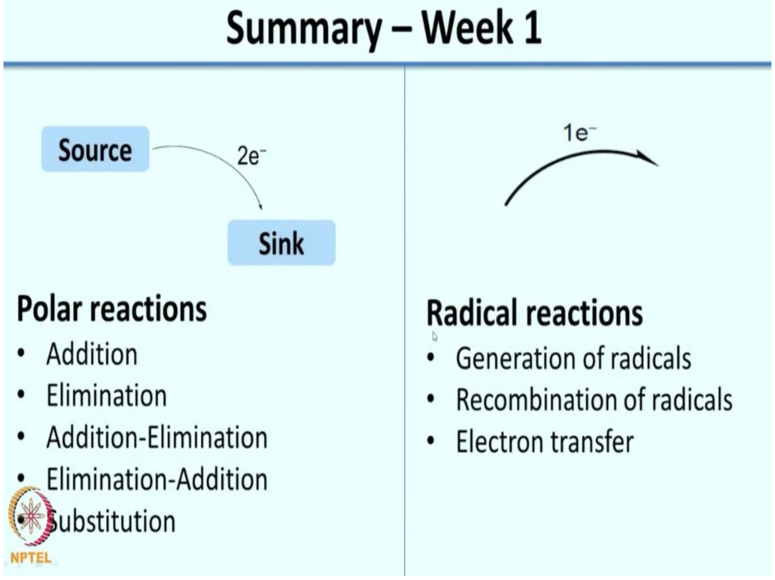

Summary – Week 1

Polar reactions
- Addition
- Elimination
- Addition-Elimination
- Elimination-Addition
- Substitution

Radical reactions
- Generation of radicals
- Recombination of radicals
- Electron transfer

one is the polar reactions and the second is the radical reactions. So, for polar reactions what you do is you use a double headed arrow to show movement of electrons and this double headed arrow indicates movement of 2 electrons. So typically, the arrow originates from the electron source and it goes to the electron sink. So, lot of terms that are used analogous to source is a donor and nucleophile and instead of a sink you would have heard terms like electrophile and acceptor.

Then we also looked at a quick recap of the different types of reactions you have under polar reactions, so you have addition reaction, elimination reaction, addition-elimination, elimination-addition and the substitution reaction. The next thing you looked at was radical reactions. Now in radical reactions the main difference is that you use the single headed Arrow. In some books it is also called as a fishhook arrow.

And this arrow indicates movement of a single electron and in radical reactions typically what you have will you have the generation of radicals, you have recombination of radical and then you have the process of electron transfer. So, we also looked at some problems where you were made to write reaction mechanism for polar reactions or radical reactions.

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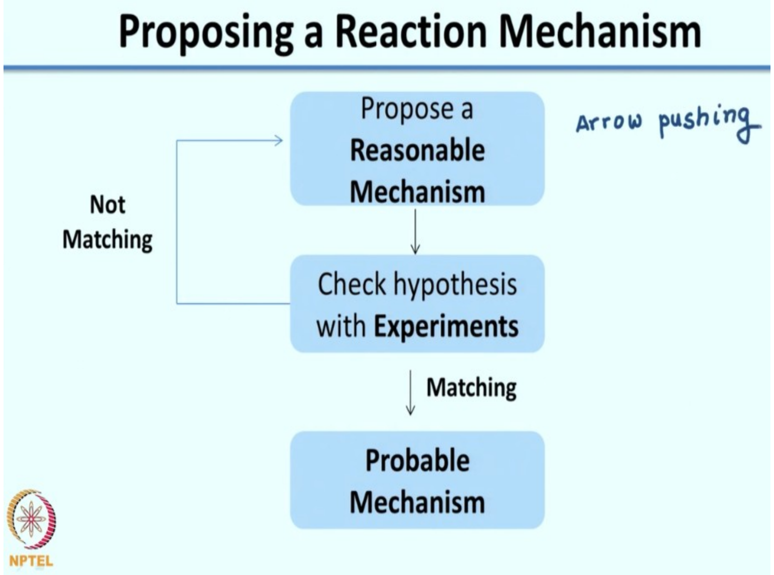

Proposing a Reaction Mechanism

So now coming back to what we had started off in the beginning of this course. So what I told you is in this course what you will be able to do is to be able to propose a reasonable reaction mechanism and then you should be able to check hypothesis by designing experiments. So just as I said you can propose anything you want, but then to ensure that whatever you have proposed makes sense you would need to prove it using suitable experiments.

So in the last week we had looked at how to write reaction mechanisms. Now what we would look at is we had looked at the arrow pushing.

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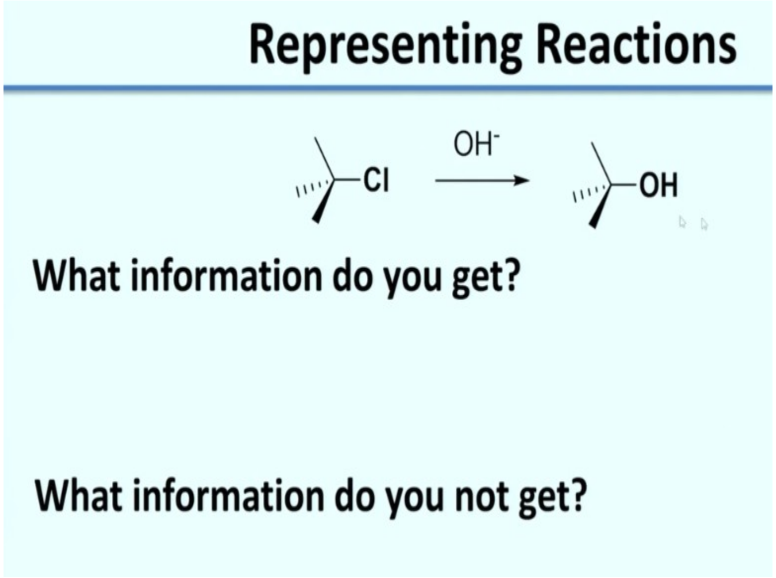

Representing Reactions

What information do you get?

What information do you not get?

So what are the ways of representing reactions? Now the simple way shown here is a reaction where you have a substitution taking place. So you have a chloride being replaced by an OH and now your nucleophile here is OH$^-$. So, based on what you learnt in the previous week you should be able to draw an arrow pushing mechanism for this. So now what I would like you to do is I would like you to think on 2 questions.

One is when you just look at the reaction being expressed in this way where you have A going to B which is the reactant going to product and then you have the reagents given above the arrow, 1) what information do you get when you look at this, 2) what information do you not get. So I would like to spend a couple minutes to think about these questions and write down on a sheet of paper your thoughts.

So you can press the cause button on the video and think about these 2 questions. So to repeat what information do you get and what information do you not get when you look at this representation of writing reactions? So now you can compare whatever we have with answers on your sheet.

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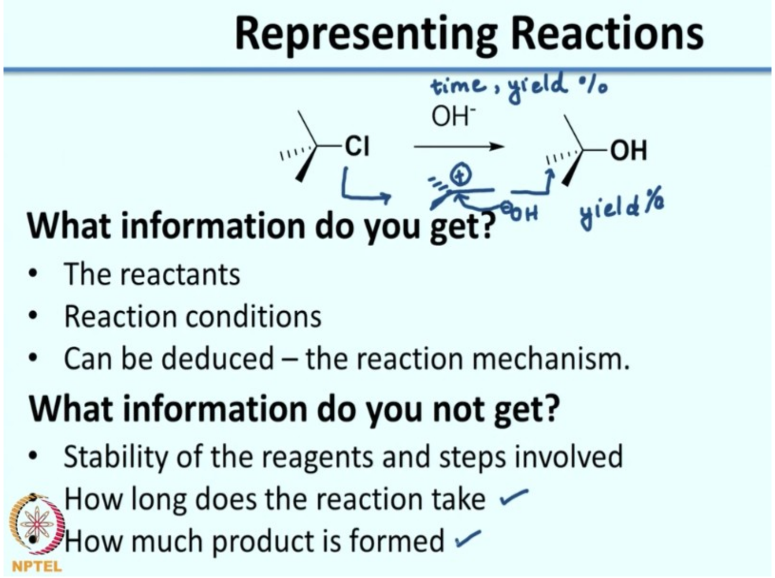

Representing Reactions

What information do you get?

- The reactants
- Reaction conditions
- Can be deduced – the reaction mechanism.

What information do you not get?

- Stability of the reagents and steps involved
- How long does the reaction take ✓
- How much product is formed ✓

The information that you do get when you look at this representation is, one is straight forward you know what the reactants are- so by looking at this you know the reactant is a t-butyl chloride and the other reactant is OH^-. You know the reaction condition, so in this way in this case you know it is a basic reaction. A lot of time they there will also be information as to the solvent used for the reaction, the temperature used for the reaction

which is very important for you to understand which mechanism is taking place and we will look at all of these effects later like how the solvent effect the reaction, how the temperature effects the reaction. Now what is not immediately apparent but can be reduced when you look at a representation like this is you can reduce the reaction mechanism and we looked at that last week. So, with this representation you would get some idea about what could be a possible reaction mechanism.

Now what is the information that you do not get? What you will not understand is stability of reagents. So, stability is in general correlated with energy. So, you do not know how stable or how unstable a reactant or the product is and you also do not know going from this to this what are the steps involved. Now based on what we have studied last week this mechanism would probably be an S_N1 mechanism.

So because it is an S_N1 mechanism what you would have is, you would have the first step which is generation of the carbocation and then in the second step you would have OH^- come in to give you the product. So, this information you can deduce looking at the arrow going from A to B, but you will not be able to clearly say that this intermediate is formed. So the reaction does not tell you stability of the intermediates or the reagents and the steps involved.

It also does not tell you how long the reaction takes. So the reaction can take 30 minutes, it can take 1 hour, it can take 2 days, this information is not clearly apparent. The other thing is you do not know how much product is formed. So sometimes when people use this representation for reaction, what they do is they give you the time also above the arrow and they also give you the yield which is represented in terms of percent.

Sometimes the yield is also written below the product. So if this information is there you would know how long the reaction took and you will also know how much product is formed. But now let us look at the first part which is stability of the reagents and steps involved. So we will look at multiple ways of representing reaction. So one way was in terms of the actual changes taking place in the molecule in terms of structure.

The other thing is what is called as a reaction co-ordinate diagram and you must have come across this earlier.

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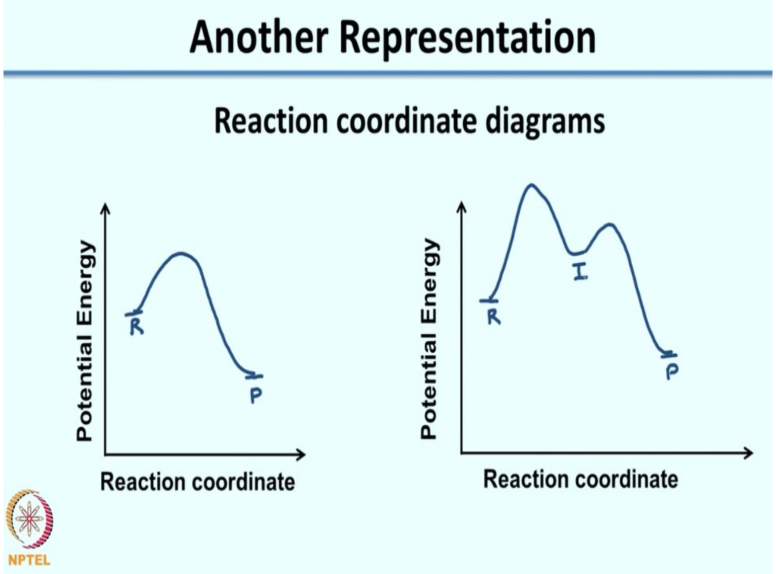

Another Representation

Reaction coordinate diagrams

So the reaction co-ordinate diagram typically has your Y-axis which is the potential energy and the X-axis which is called a reaction co-ordinate and what you would see is you would have things which look like this, you would also have reaction co-ordinate diagrams which look like this. So, as you can see both of these diagrams look very different and you can have multiple reaction co-ordinate diagrams.

And we will look at these in the due course of this week. So now when you look at a diagram like this what exactly does it represent? So there is lot of information that is actually stored in a simple diagram shown like this. So in order to understand information it is very important that we actually get an idea of what all the terms here mean and what is the physical significance of the Y-axis and the X-axis.

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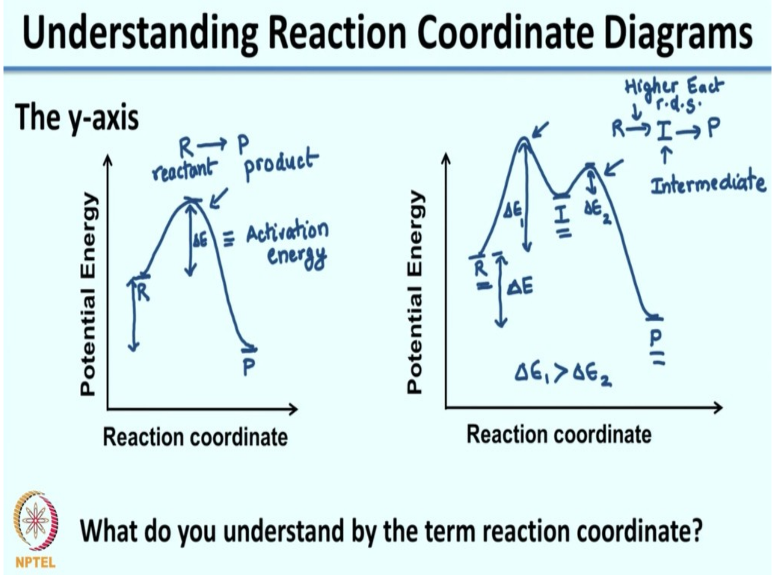

Understanding Reaction Coordinate Diagrams

The y-axis

What do you understand by the term reaction coordinate?

So coming to the Y-axis it is the potential energy, so when I write for example, when I am writing a reaction co-ordinate diagram, I will again look at the case I had shown in the previous slide, so I have the diagram which looks like this, so your Y-axis gives you the potential energy. So what you can see from this is that if I come R versus P, you can look at the energy difference and you can say R has more energy than P.

And then what you would see is typically you would see a mix of hills and valleys. So this is one case, the other case which I had shown is, so in this case what you see is here you have 1 hill whereas in this case you have 2 hills. So what exactly do these hills mean? So we are looking at the Y-axis which is energy, so based on the Y-axis one thing that you understand is when you are going from this R to this P you need to cross 1 hill, when you are going from this R to this P you need to cross 2 hills. Correct?

Now what is this I and what exactly do these hills mean? So, as you can see from the Y-axis just the fact that you are talking about a hill, you know that the energy of this hill is higher than R and P. Similarly the energy of both of these hills is higher than R, I and P. Now what this represents is a reaction given by R going to P, whereas this represents a reaction given by R going to I, going to P. I is your intermediate.

And by now if you have not understood R is your reactant and P is your product. So looking at your Y-axis you have an idea of the relative energy of R and P. So in both these cases you have R which is at higher energy than P and what you would see is if you look at the 2 hills, so this is the energy difference between R and the hill in the first case. In the second case what you would see is when you compare the 2 hills you can imagine yourself climbing from R over this hill coming to I which is a valley climbing another hill to P.

So when you look at this figure which is the hill that would take you more effort to cross? So as you see is ΔE1 is greater than ΔE2, what you would see is to cross the first hill would involve more effort. It would involve more time. So in terms of chemistry with ΔE could be equivalent to your activation energy for a reaction. Now based on the first reaction what you see is you just have 1 barrier to cross, so only one activation energy that you need to overcome.

So what you understand here in this case is that this is a single step reaction. In the second case you have to cross 2 hills out of which the first hill is the larger hill, so it has the larger activation energy, so lot of times this corresponding E activation. So this would correspond to the rate determining step or RDS. So, such a simple graph can give you lot of information with respect to the energetics of a reaction which was missing when we were talking about reaction mechanism.

So looking at the reaction coordinate diagram the information you get is you get information about the energy of your reactant, your product, you get information about what all intermediates are present and the relative energy of the intermediate with respect to your reactant as well as the product. So now you have a fairly good idea about the Y-axis. Now let us try to understand what exactly do you understand by the term the reaction coordinates.

So again I would like you to press the pause button on the video and look at these graphs carefully and think what do you think the reaction co-ordinate actually means? What does it signify? What property of the reaction are you talking about when you talk about reaction coordinate? So whatever you have written I would like you to set aside in your sheet of paper or in your notebook.

And then once I explain this you can go back to it and change whatever you had written or may be you would not need to change because whatever you have written it correct. So understanding the reaction co-ordinate is extremely important because then it makes it very easy for you to understand a lot of the principles that are associated with physical organic chemistry.

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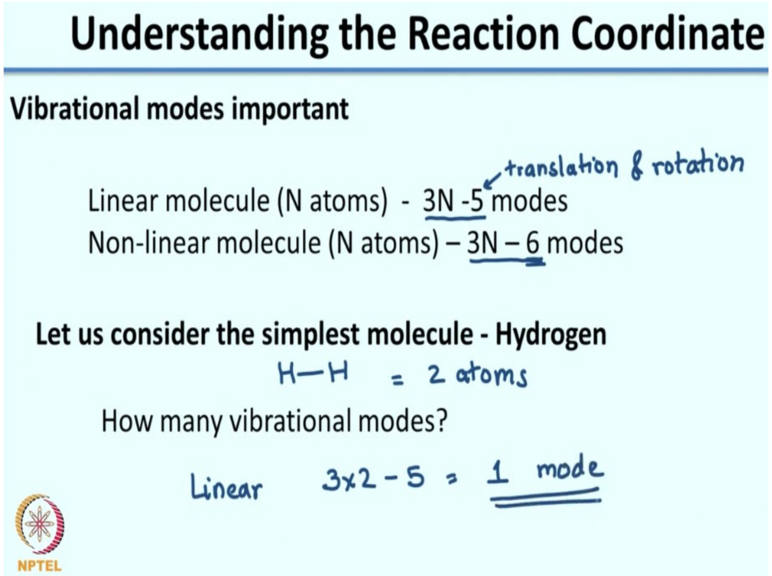

Understanding the Reaction Coordinate

Vibrational modes important

translation & rotation

Linear molecule (N atoms) - $\underline{3N-5}$ modes

Non-linear molecule (N atoms) – $\underline{3N-6}$ modes

Let us consider the simplest molecule - Hydrogen

H—H = 2 atoms

How many vibrational modes?

Linear $3 \times 2 - 5 = \underline{\underline{1 \text{ mode}}}$

So when you need to understand the reaction co-ordinate, what you need to understand is reactions involve formation and breaking of a bond. So if I consider this to be a bond, this would be breaking of a bond, this would be formation of a bond and when I talk about breaking and formation it would involve stretching of this bond and compression. So when you talk about stretching and compression the mode that comes in your mind is a vibrational mode.

When you consider any molecule the molecule is comprised of N atoms. Now each atom would have its 3 degrees of freedom. So what would happen is if you have a linear molecule or a non linear molecule, let us look at both of these cases and how the vibrational modes will differ in each of these cases. So let us imagine a molecule with N atoms, so as I said it would have 3N degrees of freedom out of these the 3N would be a mix of translation.

It would be a mix of translational, rotational and vibrational degrees of freedom. So when you talk about say a linear molecule or a non linear molecule, when you talk about translation it can move in the X, Y or Z axis, so that takes care of 3 degrees of freedom. So that is 3, other than translation what the molecule can do is it can rotate, right? So if you have a linear molecule it can rotate along its own axis which is like this. It can also rotate along this plane, that is one mode and then it can rotate along this plane which is the third mode.

So again, to repeat, when you talk about rotation it could be along the axis of the molecule, it could be along this plane and it could be along this plane. Now what happens is, for a linear molecule when it rotates along the axis essentially there is no change. So, you essentially have 2 modes of rotation. So that is why the total number of translational and rotational modes for a linear molecule is 5- 3 for translation and 2 for rotation.

So what is left over for vibration would be 3N-5, because 3N is total degrees of freedom and 5 are gone for translation and then rotation. Now in a non linear molecule what happens is it still has the 3 modes that are possible for rotation, because now if you rotate along the axis of the molecule it does not remain unchanged. So you have 6 modes and the total number of vibrational modes are 3N-6.

So now let us considere the simplest molecule, so let us consider hydrogen. Again I want you to think about how many vibrational modes are present for hydrogen. You can press the pause button. So now hydrogen has 2 atoms, it is a linear molecule, so it will have, so it will have 1 mode and like I showed you with this pen it is essentially the stretching mode. So it has one vibrational mode if I plot the potential energy versus the distance between the 2 atoms which is R.

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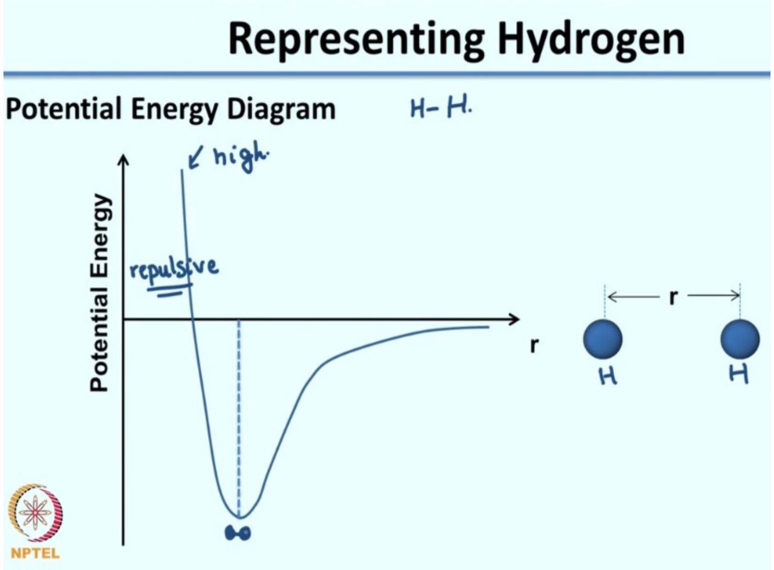

Representing Hydrogen

Potential Energy Diagram

So here I am plotting the potential energy versus the distance between the 2 hydrogen atoms. So when the distance is very very small, so you have these 2 atoms very very close to each other, you have highly repulsive forces. So what happens is the energy is very high. Now as the distance increases, it comes to an optimal distance, this is probably where you have the constructive overlap of the hydrogen atomic orbitals to give you the hydrogen molecule.

So this is the optimal distance where you have the lowest energy and then once, as you start pulling the 2 atoms away and as the distance goes on increasing, this stabilization is lost and then the energy goes on increasing and then it tapers to the point where you can equate it to where the energy would be equal to 2 hydrogen atoms which are essentially at an infinite distance or far away from each other.

So this is what the graph looks like. So when you look at this graph, do you see a correlation with your reaction co-ordinate diagrams? So you have a potential energy and on your X-axis what you are thinking of is the distance between the 2 hydrogen atoms. So what I am trying to the point I am trying to make is when you look at a reaction coordinate diagram the X-axis essentially gives you an idea about the bonding changes that take place or the changes in the geometry of the molecule.

So, it looks at what are the bonds, what are the changes that take place in the geometry or the bonding of the molecules as the reaction takes place. So remember it has nothing to do with time, all it tells you is the change in the bonding or in some cases you can think of it as a geometry parameter. So now with hydrogen case it is actually very very simple.

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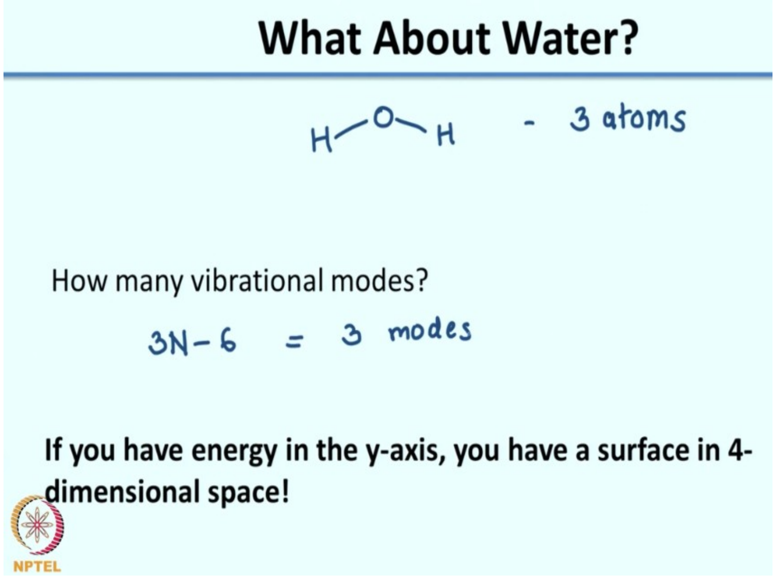

What About Water?

H–O–H - 3 atoms

How many vibrational modes?

$3N-6 = 3$ modes

If you have energy in the y-axis, you have a surface in 4-dimensional space!

Let us now look at the next case where we have water. So now water is you have 3 atoms, if you think of it water is much simpler than most of the reactions we saw in the earlier week, right? And it is either a solvent or we use it either to abstract a proton or in some cases we also used it as reactant. So it has 3 atoms and it is a non linear molecule, so how many vibrational modes? So in this case it would be 3N-6, so that would be because N is3.

So now if you were to represent water, imagine using a similar potential energy diagram, you are talking about 3 modes of vibration and then on the Y-axis if you have energy, you are talking about a 4 dimensional space which is very difficult for any of us to even visualize. So what is typically done is to understand reactions you can look at it as a potential energy surface.

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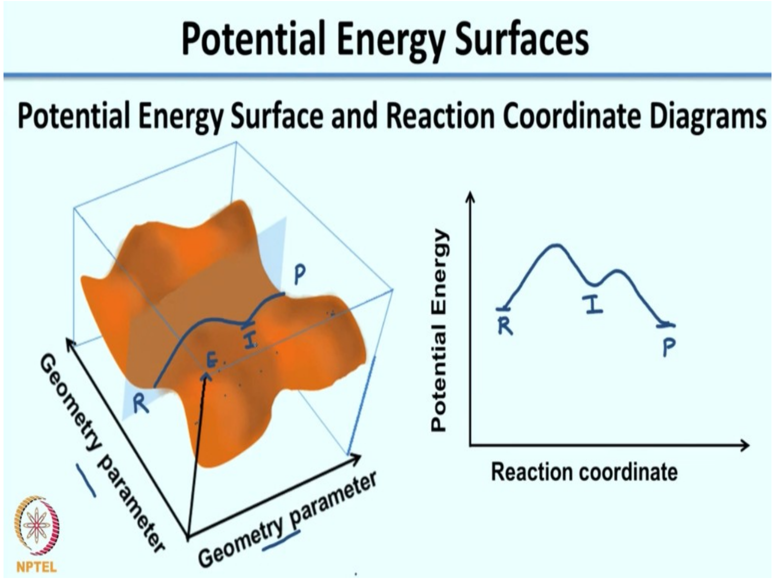

Potential Energy Surfaces

Potential Energy Surface and Reaction Coordinate Diagrams

So now so what your potential energy surface is, on this axis you have your energy and on the X and Y axis on Z-axis your energy and on X and Y axis you pick certain parameters you cannot pick all the vibrational modes and these parameters are your geometry parameters analogous through a reaction co-ordinate. So if you look at this complex surface what you would see is this complex surface has multiple hills and multiple valleys. Alright?

So imagine if your reactant is somewhere here and your product is somewhere here, so if you want to go from your reactant to your product there are so many path ways you can take. You can go along any of these pathways. You can go along this hill, so you will go along this hill, you can go along this hill but molecules are like us. So they would do what is the least energy pathway. So what they would choose would be a pathway where they have to encounter the smallest hills.

So the pathway the take to look something like this because in all of these pathways you have much larger hills. Now what essentially a reaction co-ordinate diagram is, it is imagine that you have this big surface, you can imagine it as a large cake with lot of hills and valleys, imagine cutting that with a knife. So what the reaction coordinate is is, it is the cross-section that you see. So in this case your reaction coordinate diagram would look something like.

And this here corresponds to your intermediate, so what I would like you to do now is I would like you to think about this because it is quite a complex property that we it is quite a complex concept but it is actually not that difficult if you simplify it. If you tried to imagine the potential energy surface it will be very difficult for us to do that for a particular reaction. So there are computers now that are actually used to compute the potential energy surface for a reaction.

So we cannot do it or visualize it ourselves, the computer can give us an output like this and looking at it one can figure out what would be the least energy path. So what an essentially telling you is you do not need to construct all the hills and valleys, sort of like going from Mumbai to Pune you do not have to actually build the mountains and the valleys you already get that if you look at a map all you need to figure out would be what would be the shortest way to go from Mumbai to Pune which also the map gives you.

But you need to be able to do is you need to be able to read that map. So in this case the best way for you to reach from the reactant to product would be via this path way.

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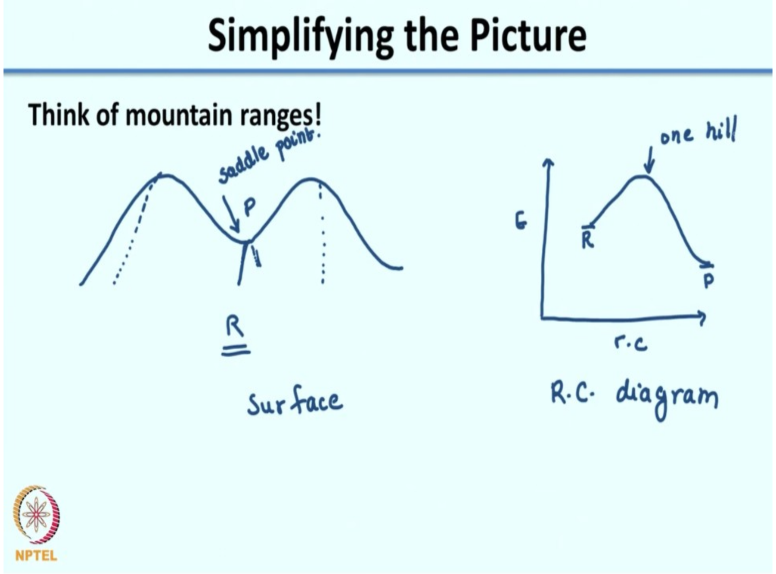

Simplifying the Picture

Think of mountain ranges!

Now I would like to simplify this further instead of using a very complicated diagram I will try to draw one yourself, I will try to draw one myself, so think of just 2 mountain ranges, so I have this 1 mountain range and I have a second mountain range. On this side I have my reactant and on the other side of my mountain range I have product. You can also as I said think of this reactant as Mumbai and your product as Pune.

So you imagine you have multiple ways to go from the reactant side to the product side. So if I go via this pathway it will be very very long. I have to climb this big hill. If I go along this path way also there will be a big hill. So there are multiple pathways if you see I can take. The quickest or the least energy pathway would be one where I go from where I go through this valley. Alright?

So if I were to translate that to a reaction co-ordinate diagram, as I said it would be a slice between the 2 mountains, so I would have reactant going to product. And in this case I just have a single small hill that it needs to a single small valley that it needs to cross. So this would be the surface and this would be the reaction coordinate diagram. So what you need to understand is what actually looks like a valley on your potential energy surface would be your hill in a reaction co-ordinate diagram.

So this point is also called as the saddle point. So I have tried to simplify the potential energy surface by thinking of it as going from point A to point B as I said you can think of going from Mumbai to Pune. This would be the best pathway which is the path reaction will take and you represent that as a reaction coordinates by essentially imagine that your slicing it here and drawing, drawing this map route.

So you are actually drawing this map route in reaction co-ordinate diagram and in this case you have only one hill unlike the previous case which I showed on the earlier slide where you had 2 hills. So this is a much simpler representation of a reaction co-ordinate. So now if you see there are 2 things that show up when you look at a reaction co-ordinate.

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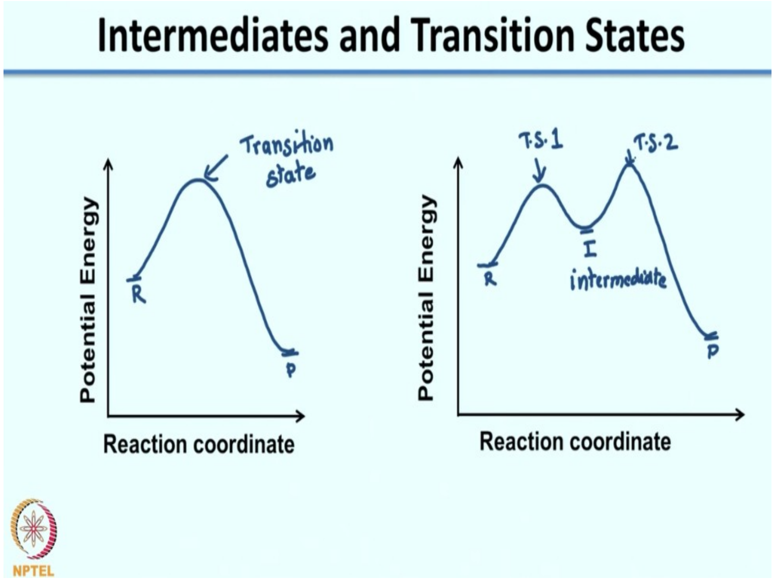

Intermediates and Transition States

So you have the 1 hill case that I looked at earlier and then you had the 2 hill case. So what do these hills and valleys mean? The hill here corresponds to what is called as a transition state and the valley corresponds to the intermediate. So, in this case you have 2 transition states, you have transition state 1 and transition state 2, it is very important that you understand the difference between an intermediate and transition state.

So when we come back again in the next lecture we will again look at reaction coordinate diagrams and you will look at what you mean by intermediates and transition state. But before I go I would like you to think about these 2 questions. Now that you have a rough idea of what reaction foreigner diagrams mean.

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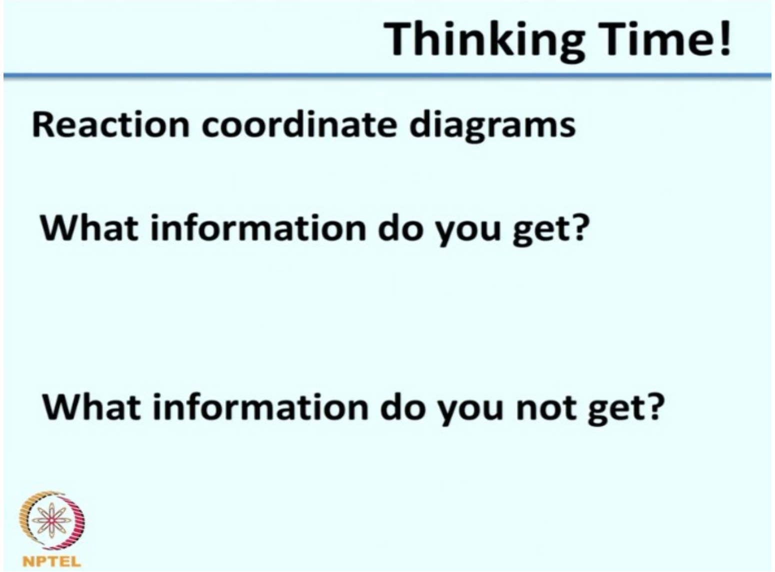

Thinking Time!

Reaction coordinate diagrams

What information do you get?

What information do you not get?

I want you think about these 2 questions a) what information do you get looking at reaction co-ordinate diagrams and b) is what information do you not get when you look at reaction co-ordinate diagrams? So think about these questions and we will look at them when we come back to the next lecture. Thank you.