Mechanisms in Organic Chemistry
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Lecture-06
The Hammond Postulate

So welcome to the second lecture of this week. In yesterday's lecture we had looked at representing reactions using reaction coordinate diagrams.

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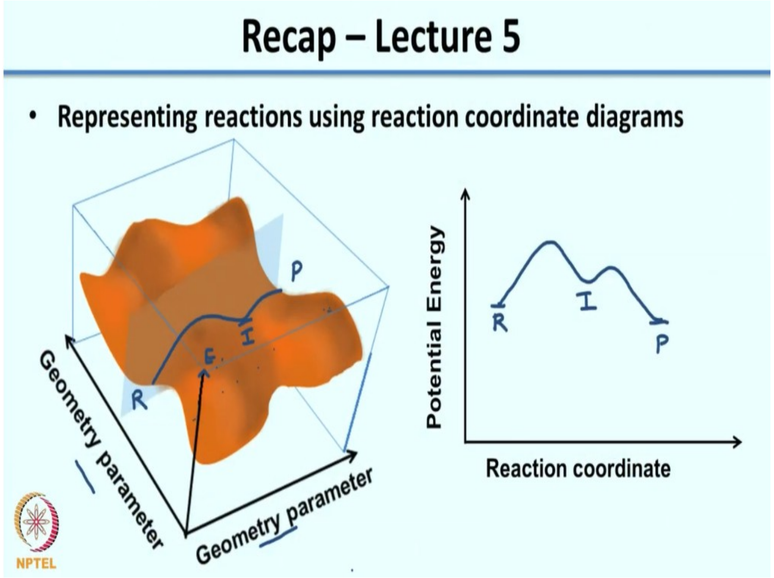

Recap – Lecture 5

- Representing reactions using reaction coordinate diagrams

And I told you that in general whenever you have a reaction, the overall reaction can be expressed in terms of a potential energy surface. Now the surface looks pretty complicated, but to simplify it we use what is called as a reaction coordinate which is the cross-section of a potential energy surface and now in the reaction coordinate diagram your Y-axis corresponds to the potential energy and the X-axis corresponds to the reaction coordinate and the reaction coordinate is essentially a geometry parameter which indicates the change in the bonding of the molecules.

So, it could be associated with bond breaking, bond breaking, bond making, so essentially reaction coordinate is a geometry parameter and the Y-axis is the energy parameter. So now with this concept I had asked you to think about this question looking at reaction coordinate diagrams what information do you get.

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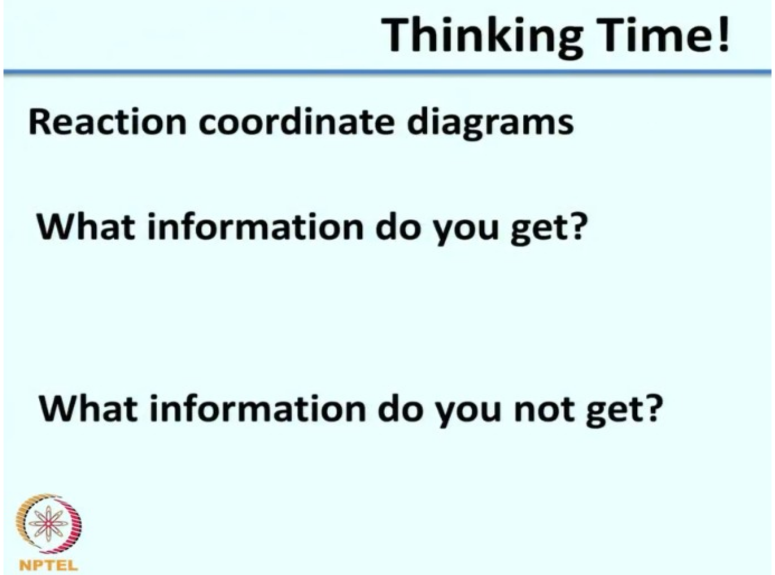

Thinking Time!

Reaction coordinate diagrams

What information do you get?

What information do you not get?

And what information do you not get?

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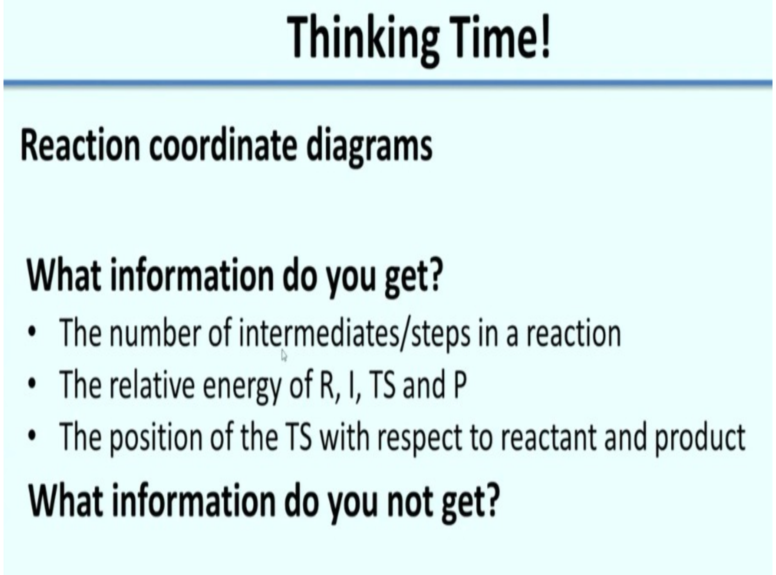

Thinking Time!

Reaction coordinate diagrams

What information do you get?

- The number of intermediates/steps in a reaction
- The relative energy of R, I, TS and P
- The position of the TS with respect to reactant and product

What information do you not get?

So some of the information that you get using these reaction coordinate diagrams is, unlike just showing the reaction with an A going to B arrow representation, in the reaction coordinate diagram you can see the number of intermediates or steps involved in a reaction. Also the reaction coordinate diagram, since you have the Y-axis as energy gives you the relative energy of the reactant, the intermediates, the transition states and of course the product.

So you can compare the relative energies of all these species and the other thing which the reaction coordinate diagram tells you is the position of the transition state with respect to the reactant, product and intermediate. So I would hold on regarding this question as to what information you do not get because although I have listed out all these things that you get from a reaction coordinate diagram.

It is very important to see the meaning behind all this. So what can you do by understanding the relative energy of say R, I, TS and P? What do you understand by the position of transition state? So by looking at the position of transition state is there some information that you can get about the reaction? So let us try to get more details on these points before we get to the point as to what information you do not get.

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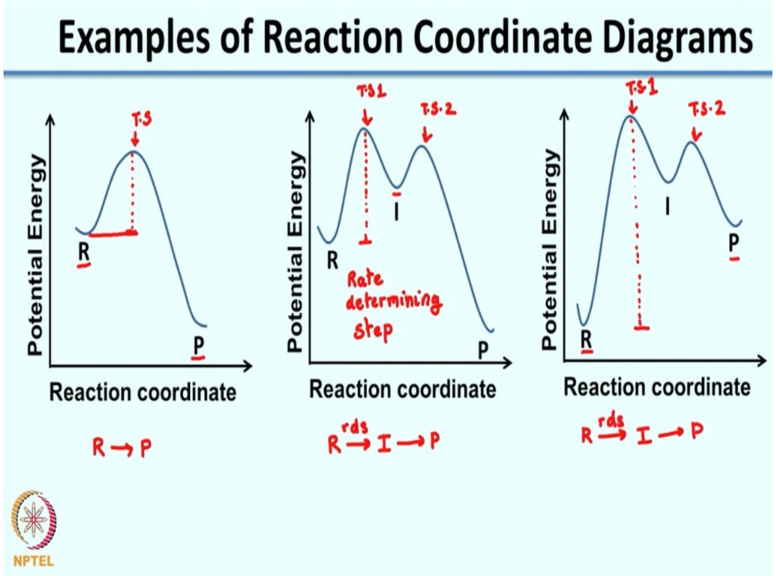

Examples of Reaction Coordinate Diagrams

So these are some examples of reaction coordinate diagrams and what I would like you to do is I would like you to do a small exercise, so you can on each of these reaction coordinate diagrams the first thing is on your notebooks you draw each of these diagrams so that they look exactly as seen on your screen. You can pause this video. Okay. So now assuming you have drawn these reaction coordinate diagrams, what I would like you to do is I would like you to label the reactant as R the product as P and the intermediates as I in each of these reaction coordinate diagrams.

So you can again press the pause button and do the small exercise. So hopefully by now you have labelled the reaction coordinate diagrams and your labels should look something like this. So in each case what you have is, so you have your reactant, product and as I told you in the last class the hill corresponds to a transition state. So, in the first case what you see is you have a simple reaction of R going to P.

It looks simple on the reaction coordinate, it might be quite complicated, but by simple what I mean this it has only 1 hill or 1 transition state to cross. So this reaction can be represented as R going to P. Now in the second case what you see is you have 2 hills. So this reaction has 1 intermediate and in the second case also the reaction has 1 intermediate and you have 2 hills corresponding to transition state 1 and transition state 2.

Now what I would like you to look at is I would like you to look at now the relative energy levels of the reactants and the products and the intermediates and the transition state and try to understand what information you are getting by looking at these energy levels. Again, you can press the pause button and think about it. So, in the first case what you see is going from the reactant to product your reactant is higher energy or less stable as compared to your product.

This is similar in the second case except that you have now an intermediate. In the third case you have the product being less stable than your reactant because it is at a higher energy. Now let us look at the energy of the transition state with respect to the reactant and you can make dotted lines to show the energy of the transition state with respect to the reactant. So, I will show this to you in the first case.

So, this is the energy of the reactant. So by a dotted line you can look at the energy difference between the reactant and the transition state. In this case you have 2 transition states, transition state 1 and transition state 2 and this is your reactant energy. So, we have drawn the energy with respect to the reactant. Now when you look at it if you compare these 2 hills, this hill is much larger than the second hill.

So if you were to compare the energy between the reactant and transition state 1 and the reactant and transition state 2, the hill that you have for transition state 1 is much bigger. So what this indicates is that, you need to have so there is a greater barrier in going from R to I. So this would be what is called as your rate determining or rate limiting step. Similarly, what you would see in this case is that you have a huge barrier going from the reactant to transition state 1.

And the barrier for transition state 2 is lesser. So these reactions can be represented as R going to I, going to P and in this case this would be the rate determining step. Similarly, you have in this case R going to I, going to P and first step would be your rate determining step. So, as you can see there is a wealth of information that you get by looking at these simple graphs, so looking at the graph you get an idea of what is the rate determining step.

You also get an idea of what are the intermediates. So I have shown examples where you have either no intermediate or you have a single intermediate. Now if you have multiple intermediates the reaction coordinate diagram will look more complicated than the ones that I have shown here. So now we will do a similar exercise. I would like you to look at these 3 reaction coordinate diagrams and then try to figure out which is the rate determining step.

And try to represent these reactions as I had shown in the previous case using R going to I, going to P as arrows below each reaction.

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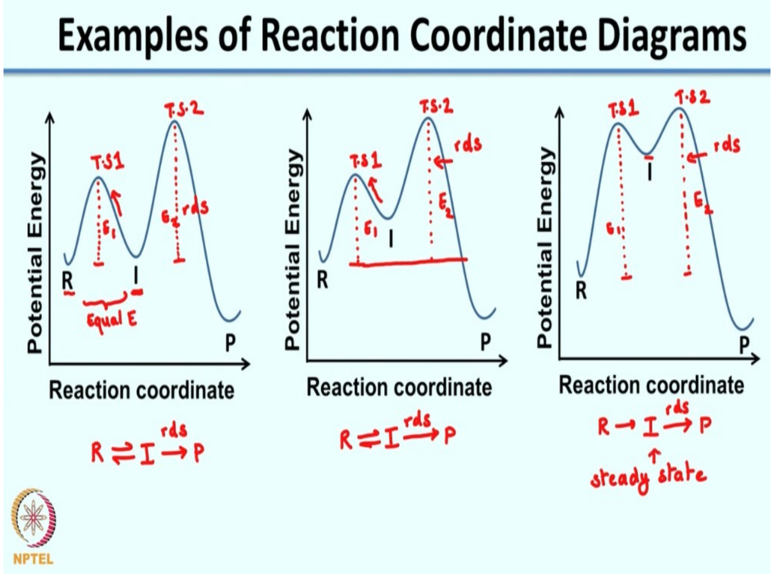

Examples of Reaction Coordinate Diagrams

$R \rightleftharpoons I \xrightarrow{rds} P$

$R \rightleftharpoons I \xrightarrow{rds} P$

$R \rightarrow \underset{\underset{\text{steady state}}{\uparrow}}{I} \xrightarrow{rds} P$

So you can press the pause button and go ahead and do this exercise. So in the first case what you would see is if I compare TS1 and TS2 so I have this is the energy for the first step, for the second step this is the energy for the second step. So in this case the energy to get to TS2 is higher than TS1. So this would be the rate determining step. Now another interesting thing that you can see from this reaction coordinate diagram.

So this is a new concept that I am going to tell you, so here what you see is once you come to I which is your intermediate the barrier for it to go to TS1, so which is this energy let us call it let us call it E1, so the energy E1 for going from the intermediate to the transition state is less than the energy E2 required to go from the intermediate to transition state 2. So, if you think of the intermediate once it is formed, energy wise the barrier for it to go back to the reactant is lesser than the barrier for it to go to the product.

So, in such cases what is observed is you would have, so you can have an equilibrium between the reactant and the intermediate before it goes to the product and the second step would be the rate determining step. So we can again get a lot of information by looking at the relative energies of each of these transition states with respect to the intermediate and the product. Now let, now look at the second example.

And using this new concept whatever answer you had written before, you can change it to make sense I mean to include this new concept. You can again press the pause button and go ahead and do this exercise. So now in this case you have transition state 1, transition state2, so this is your E1, now what you need to focus here is if I compare so this is the energy of the reactant, although the energy to go from the intermediate to transition state2 is almost equal to E1 the energy to go from the reactant to transition state 2 is significantly higher. So that is why this step is the rate determining step.

Now what about the possibility of equilibrium in this example? So in this example also what you see is that the energy to go from I to transition state 1, now in the previous case what we had is we had I and R at almost the equal energy. In this case the intermediate is at a higher energy or more reactive with respect to the reactant. So, what you would see is the barrier to actually go from the intermediate to transition state1 is less than the barrier to go from reactant to the transition state 1.

And again, this barrier is smaller than the barrier to go from intermediate to transition state2. So in this case also you have the chance of an equilibrium. And again the rate determining step would be the second one. Now the third reaction coordinate diagram is extremely interesting. So here what you have is you have an intermediate which is extremely high in energy, so again you have your transition state 1 and you have your transition state 2.

So, if I now compare the energy, so this would be E1 and if I compare now with respect to the reactant, E2 is larger than E1, so again this would be your rate determining step. Now here what is interesting is although the barrier to go from the intermediate to transition state1 is slightly smaller than the barrier to go from intermediate to transition 2, the different, transition state2, the difference is actually very less.

So what you would have is as soon as you form intermediate 1, because the barrier is so less, it would probably immediately go to the product and we will look at this later this is a situation where one gets what is called as a steady state, where as soon as you come to R, as soon as you come to I you form your product. Here again this is the rate determining step. So we will look at this later. So we will look at this later in detail when we look at kinetics of reactions. So now again when we had spoken about what information you get from the reaction coordinate diagrams.

The first 2 things we looked at when we now saw the reaction coordinate diagrams and looked at the relative energies of the reactant product and intermediate and transition state. So this relative energy gives us a lot of information regarding the type of the reaction. Now we have not yet discussed what the position of the transition state with respect to reactant, product and intermediate can tell us about the reaction.

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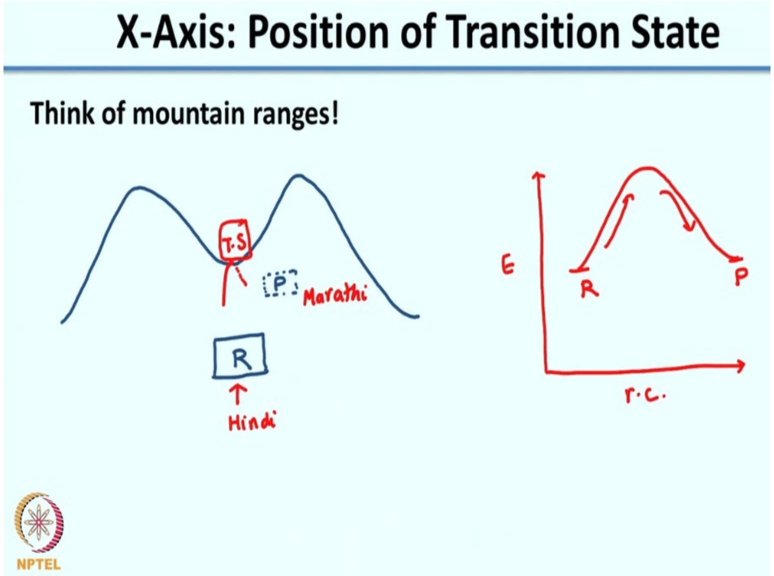

X-Axis: Position of Transition State

Think of mountain ranges!

So now let us come back to what we were doing in yesterday's class. Wahen you think of a potential energy surface you can consider it as a simple example, so I told you, you can think of a mountain range, so you have a mountain range and if you want to go from let us call this as R and on the other side of your mountain range, I am showing this as dots because it is at the back you have your P.

So you are going from R to P and you have this big mountain range in front of you, so probably the quickest path not probably surely the quickest path would be where you go via this road and then once you cross the valley you go on the other side to your product. So as I told you you can think of this as 2 cities where you are trying to go from city R to city P. Now I would like to simplify this further for you.

So the reaction coordinate for this would look something like this. So there are multiple possibilities one is that R and P are say at similar heights, so you have a situation like this. Now I would like you to think of some scenarios, let us say that in city R, alright? So now let us move really away from reactions and just think about 2 cities. So if you have city R and city P let us assume that in city R people say speak 1 language.

So we can say Hindi and then in city P let us say people speak Marathi. Alright? So this is a very common-sense kind of question so imagine that you are going from city R where you have Hindi speaking people to city P where you have Marathi speaking people. Now imagine that you do not have a scenario where you have the path being highly symmetric going from R to P. So suppose it is not as symmetric as I have shown here.

But the valley that you have you reach the valley within say 10 minutes of starting your travel from R to P and the whole journey takes you around 2 hours. So say as soon as you start from city R you have spent 10 minutes on this path and immediately you reach your valley here which is your transition state and then after a whole hour and 50 minutes you will reach city P where people speak Marathi.

So what do you think would be a greater chance, do you think there will be more people speaking Hindi or Marathi in this city that we call as TS? So again I will repeat the question you are going from city R to city P, the journey takes 2 hours but as soon as you travel for like 10 minutes you reach TS which is the valley R and or the top of your journey and after that it takes you 1 hour 50 minutes only to reach P.

So what do you think the people who live in the city TS, will they be speaking more Hindi or more Marathi? Logically what one would think is when you are closer to city R the characteristics of city R would be seen more in the city transition state or TS. So there is a greater chance that people will be speaking Hindi in TS and not Marathi. So using the same logic, imagine you have a reactant undergoing some bonding changes to form the product. Right?

So once the reactant undergoes some bonding changes and it would reach the transition state if the energy of the transition state and the reactants are very close to each other that means the reactant did not have to reorganize much to form the transition state or in other words it means that the transition state would resemble the reactant just like our city TS had more Hindi speaking people as opposed to Marathi speaking people.

So this concept is essentially what is called as a Hammonds postulate and if you understand that the reaction coordinate essentially has to do with geometry what is now going to be very clear for you is that Hammonds postulate is actually something which is very logical.

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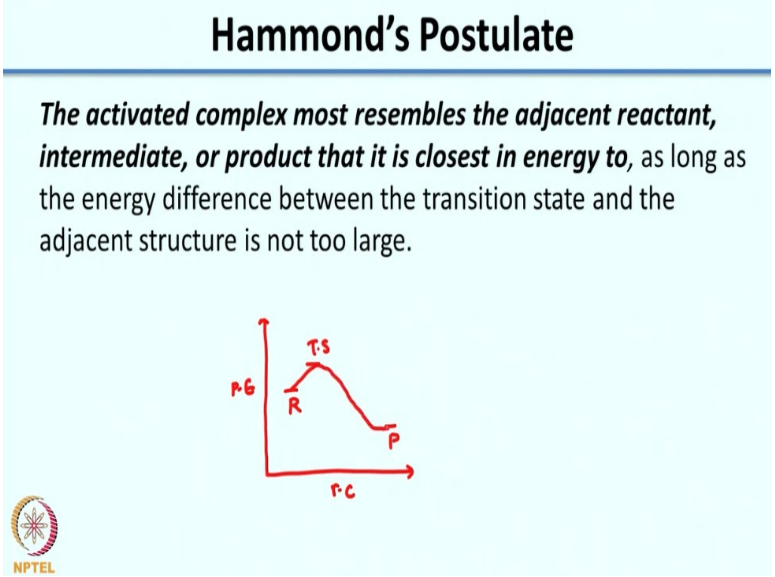

Hammond's Postulate

The activated complex most resembles the adjacent reactant, intermediate, or product that it is closest in energy to, as long as the energy difference between the transition state and the adjacent structure is not too large.

So what the Hammonds postulate states that states is that the activated complex most resembles the adjacent reactant intermediate or product that it is closest in energy to, as long as the energy difference between the transition state and the adjacent structure is not too large. So what it tells you is that if you have the transition state energy very similar to the reactant energy it would resemble the reactant more.

If the transition state energy is very similar to the intermediate energy it will resemble that more. Which as I said, which is very logical because if I look at my potential energy diagram and I am going from my reactant to my product, if my transition state is very close to the reactant in energy, what it indicates is that there are there is not much of difference in what the reactant and the transition state looks like in terms of bonding. Remember the reaction coordinate indicates a geometry parameter.

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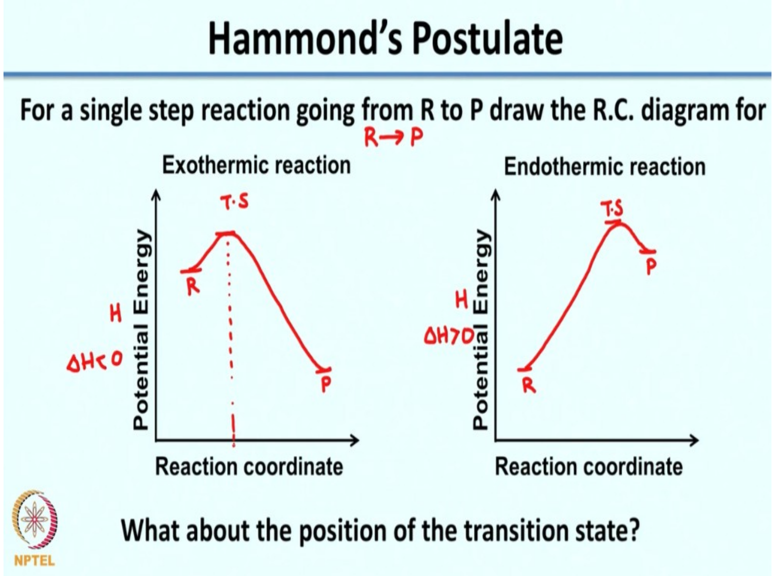

Hammond's Postulate

For a single step reaction going from R to P draw the R.C. diagram for

What about the position of the transition state?

So now I would like you to do 1 more exercise, so let us assume we are talking about a single step reaction. So a single step reaction means R going to P. So for this single step reaction what I would like you to plot is what the reaction coordinate diagram will look for A an exothermic reaction and B an endothermic reaction. So you can think of the potential energy in terms of the enthalpy which is H.

And just to refresh your memory an exothermic reaction is a reaction which gives out heat, so in an exothermic reaction what you have is you have a ΔH which is negative, whereas an endothermic reaction is one which takes up heat. So in this case you have your ΔH which is positive or greater than 0. So you can press the pause button and draw the reaction coordinate diagram for this particular case for both these phases.

So what I told you is that for an exothermic reaction the ΔH is 0, so what that indicates is that your reactant I mean the ΔH is less than 0 or negative, so what that indicates is that your reactant would be at a higher energy as compared to your product. Now for an endothermic reaction what you have is you have your reactant at a lower energy than the product. As I told you the ΔH is positive.

So these 2 things you should have been able to write based on the definition of ΔH being negative in one case and ΔH be positive in the other case. So now the question is what would the transition state look like. So when you have something which is so high energy, the logic is that there would be a very small barrier that you would need to cross to reach the product. Similarly, if your product is such a high energy product what it indicates is once you reach the transition state there is very small reorganization required to reach the product.

So in other words what it indicates is that your reaction coordinate would look your reaction co-ordinate would look something like this, remember now we are also paying attention to the X-axis. So now what you see is now that I have drawn the transition states what can you comment about the position of the transition state? So now we are looking at the X-axis, so in terms of energy I had told you ok transition state is close in energy to R, transition state is close in energy to P.

But now I want you to look at each of these graphs and try to focus on the X-axis, so, when I say focus on the X- axis what I would need you to do is essentially think of where it actually comes on the X-axis in both these cases. So 1 case what you see is it is closer to R in the other case it is closer to P.

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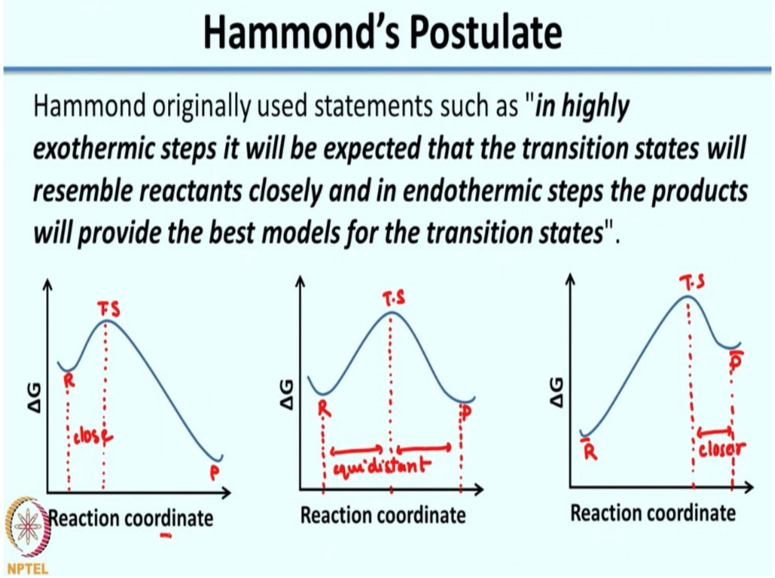

Hammond's Postulate

Hammond originally used statements such as "*in highly exothermic steps it will be expected that the transition states will resemble reactants closely and in endothermic steps the products will provide the best models for the transition states*".

So this is the definition another definition of the Hammond postulate, what it says is that in highly exothermic steps it will be expected that the transition states will resemble reactants closely and in endothermic steps the products will provide the best models for the transition states. So this is essentially the exercise that we had done in the previous slide. So now what it essentially tells you is that if you have a reactant and a product.

And you have a high-energy reactant here, the transition state will resemble the reactant more, so in terms of the X-axis, what you can see is that it is closer to the reactant. When you have R and P which are equal in energy, what you would have is, if you look at where the transition state cuts the X-axis, what you would have is they would be almost equidistant. So, it is a symmetric transition state.

In the third case where you have a high energy product and this is your transition state, now again you look at where it goes to the X-axis, what you would have is that you would have the transition state closer to your product and again what I want to emphasize is in the X-axis if it is closer it means that the geometry the bonding is very similar in the transition state and the product in this case.

So that means the product would be a very good model to understand the transition state whereas in this case the reactant would be a very good model to understand the transition state. So this is the Hammond's postulate.

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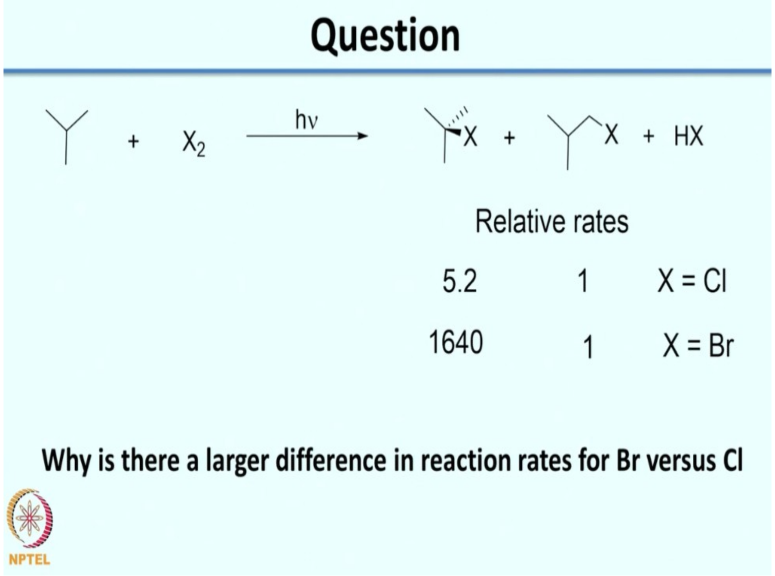

Question

Relative rates

5.2	1	X = Cl
1640	1	X = Br

Why is there a larger difference in reaction rates for Br versus Cl

And what I would like to leave you with is again a question, where the Hammond postulate actually can be seen. So, this is a free radical halogenation reaction, so you have a molecule like this and you are doing the free radical halogenation, the products that you get can be, so remember first thing you would need to do is 1) write mechanism. So, if you write the mechanism you can look at the part in the last week where we looked at mechanisms of reactions.

So, I would like you to write the mechanism for these reactions where you should be able to explain how each of these products is formed. Now what is a curious observation is that when X is chloride the rates are almost similar or the difference is less. But then when X is Br what you see is that you have a much larger rate for formation of product A as compared to product B.

So for the next lecture the homework that I would like you to do is, I would like you to write the mechanism and think about this question as to why there is a larger difference in reaction rates in the case of Br as compared to Cl and we will be looking at this in the next lecture. So thank you.