Mechanisms in Organic Chemistry
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Lecture - 9
An Introduction to Reaction Kinetics

So welcome back to the course on reaction mechanisms. So we will do a recap of the previous lecture.

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In the previous lecture, we had looked at the Curtin-Hammett principle and what the Curtin-Hammett principle does is when you have the possibility of two different products say P_B and P_A from 2 different conformers A and B, the Curtin-Hammett principle tells you what dictates the product ratio. So according to the Curtin-Hammett principle the product ratios depend mainly on the difference in activation energies for both of these reactions.

So, in the case where you have a greater difference in activation energy you would see that the product which reacts faster, the conformer which reacts faster will give you the corresponding product. So essentially product ratios do not depend on ground state energy so they do not depend on energies of A and B or P_A and P_B here. Product ratios are determined more by the transition state energies.

So it is mainly kinetics driven and we had looked at the example of the epoxidation reaction and before the end of the class I had given you this problem and asked you to think about it as to why this reaction is much slower than the reaction where you have Br coming up and OH going down, which we had discussed in the previous class.

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So now to understand this, we would need to again write the conformation for this because Curtin-Hammett principle involves the two conformers A and B. So let us try to write this. So as I told you in the last class, hopefully you have practice now writing the chair form. So if you write the chair form for this, so this is a chair form Me is going up and then H is coming down. So now we have Br coming down, so Br coming down means it is equatorial and we have OH coming up.

So what you see is in this particular molecule, you have such a situation and with these decalins, these are called decalins, the conformation is locked because the ring cannot flip, so you cannot go easily from the diequatorial to the diaxial orientation.

So now let us see if you need to do the epoxidation reaction the molecule needs to undergo some change so that you can get antiperiplanar orientation. So now in order to get the OH and Br antiperiplanar, let us try to draw it such that there is a small change in the conformation. There is not much change in the second ring. So, what you see is now you have a conformation which is sort of like a boat like conformation but it gets the antiperiplanar orientation between the OH and the Br.

Now if I were to compare these two confirmations and I compare the reaction coordinate diagram, so which of these would correspond to A and which of these would correspond to B? Which do you think would be more stable? Since you have two chair forms here, this would be more stable, so we can call this as B and this would correspond to A which is actually not very stable.

So if I were to look at the equilibrium between these two, the equilibrium would be largely in favor of conformer B, but as you can see from conformer B, it is very difficult for the epoxidation reaction to take place, so the transition state energy here is high, because it cannot have the antiperiplanar orientation, so the transition state energy is very high here. Whereas in this case although the conformation is higher in energy, so this is less stable but then because of the antiperiplanar orientation, the transition state energy is lowered.

So, one would assume that this reaction will not take place at all because you have a less reactive major confirmer, but what you observe is indeed you have the epoxidation occurring although it takes a long time. So now that you have this, it can undergo the deprotonation and you can have. So, let us go ahead and do the deprotonation in both cases. You have O^-, O^- here, you can have this coming in and the Br leaving to give you the product.

So this is a wonderful illustration of the Curtin-Hammett principle and what you see here is that the major product that you get is P_A and that corresponds to actually the less stable conformer. So this goes through the less stable conformer because the transition state energy is lowered. Now if I were to compare this with the previous reaction, in the previous reaction you had the scenario where the more stable conformer which would be B, also had the lower energy transition state.

So if you remember at the beginning of the previous lecture, we had looked at 3 scenarios and one of those scenarios is where the more reactive conformal is also the more stable conformer. So in that case you get the product much more easily. So that is why this explains why this reaction is much slower.

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There is another problem you can think about. This involves the E2 elimination reaction. If you remember the first week lectures, we had looked at different mechanisms and for the mechanism of E2, what you had seen is, for E2 again it is a concerted process, so what you need to have is you need to have again an antiperiplanar orientation. So, the dihedral angle has to be 180 degrees for the E2 elimination to take place.

So, with this information now that you have done the epoxidation where again you needed that antiperiplanar orientation, let us see if you can figure out which of these molecules will react faster. So one thing that you should understand is the relationship between these two is they are diastereomers because there is a change in configuration only at one position here. So these two are diastereomers. So, the question to you is which of these will react faster? So you can press the pause button and work out this problem and when you are back we will try to solve this together.

So now let us try to solve this together. As I said first thing you need to do is you would need to write the chair conformation for each of these. So let us do that. So let us write the chair for this. You have the isopropyl group going up and at the 2 position you have a Cl and then at the 4 position you have an Me which is going down. Let us draw it for this molecule as well. The isopropyl and the Me remain the same, so your isopropyl is going up, Me is coming down. The only difference here is that your Cl is also coming down.

So now what we need to see is which of these would undergo the elimination reaction. So the first thing I want you to identify is what is the leaving group in both of these cases? The leaving group is the Cl. So, we know what the leaving group is, which are the hydrogens that will get eliminated? If you look at the schematic I have given here, it is the hydrogen which is α to the leaving group. So now let us identify. So the hydrogen's α here are and in this case the hydrogens that you have are.

Now based on the criteria that you need an antiperiplanar orientation, what you see is in this case very nicely you have an antiperiplanar orientation of two hydrogens. So what you end up doing is you can, any of these can undergo elimination so if you have a base, I am showing you one. So what you would end up getting would be one product, which corresponds to, that would be one product, and the other product would correspond to this hydrogen getting eliminated, so what you would get is.

Now in this case what is going on, what you see with this diastereomer is that you do not have any hydrogen which is antiperiplanar. So what would you need to do, the molecule would need to flip. So when the molecule flips, so your molecule has flipped, so this is the flipped conformer of this molecule. Now when you compare these two conformers, which is more stable? As you can see in this case you have 2 axial, 3 axial substituents, so this is less stable as compared to this confirmer.

So if I were to draw the equilibrium arrow it would be largely towards the left, but then as we had seen in the case of the epoxidation, the transition state for this higher in energy and why is that? Because you are not able to get the antiperiplanar orientation. So here what you would do is, you have one hydrogen which is antiperiplanar, here this hydrogen is equatorial, so you do not have the correct orientation, so the product that you get would be this one.

So, you would get a single product here and here you will get two products. And which of these will react faster? you can think about it. As you can see here, more stable conformer is more reactive. Here what you see is, you see an illustration of the Curtin-Hammett principle. So here actually the less stable conformer is the more reactive one. So, in terms of energy what you would see is, this would be more stable. So, between these 2, the neomenthyl chloride will actually react faster. So, this is another example of the Curtin-Hammett principle.

So, based on the epoxidation reaction as well as the elimination reaction, I hope you have now a fair idea of how the Curtin-Hammett principle works. If you compare it with what we had studied earlier, the Curtin-Hammett principle mainly looks at kinetic control and among two conformers the one which has lower activation energy, is the one which will react. The ground state energies of both these conformers does not make much of a difference. So now if you remember I had asked you this question earlier regarding reaction coordinate diagrams and we had looked at what is the information that you can get from reaction coordinate diagrams.

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So, the information that you get is you know the number of intermediate steps in a reaction, the relative energy of the reactant, intermediate transition state and product and the position of the transition state with respect to reactant and product. So, the relative energy translates to the kinetic and thermodynamic control, the position of transition state translates to the Hammond postulate. Now what I want you to think about is what information do you not get from reaction coordinate diagrams.

So you have looked at so many reaction coordinate diagrams and received so much rich information from that, what I want you to think about is what is the information that you do not get? So, you can again press the pause button, think about the question and write your points on a sheet of paper. So, one of the things that you do not get from a reaction coordinate diagram is you do not get information about the time taken for a reaction to complete.

So the reaction coordinate diagram would tell you the activation energy is low or high but it will not tell you whether the reaction is done in seconds or minutes or hours because on the Y-axis you have energy and on the X-axis you have a reaction coordinate which corresponds to geometry and not the time. So, you do not know how fast the reaction is in terms of time because there is nothing there that correlates to time. So you do not know whether you have to wait for 5 days, 1 month, 1 second.

That information is not available from the reaction coordinate diagram. The other thing you do not know is again related to time, life time of the intermediates. So, when we say an intermediate is stable by looking at the energy, you do not know how long the intermediate will last, is it picoseconds, femtoseconds? how unstable or stable do we mean when we talk about these intermediates? So, time is an important parameter that you do not get from reaction coordinate diagrams.

So based on the experiments you have done in college, is there anything you are done when you are studying a reaction where you actually looked at how the reaction progressed with time. So many colleges do what is called as reaction kinetics in physical chemistry lab where you look at either change in one concentration of the reactant or the product over time and plot it. So, reaction kinetics information is something that you do not get from reaction coordinate diagrams but it is very valuable for you to understand reaction mechanisms and also to get an idea about reaction mechanisms.

So we will start with very very basic kinetics. We are not going to go into too much detail of the physical chemistry behind it, but what we will look at is how we can use it to determine the reaction mechanism.

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So single step reaction is called an elementary reaction. So let us say you have a reactant A going to the product P. So, this is an elementary reaction with one reactant. So if you were to plot the change in concentration of P over time, now initially you start with only A, correct. You are doing the reaction you have only A which is the starting material. So the concentration of P would be 0 here. Obviously you have made nothing. Now as time goes, you would be making more and more of P. So if you were to plot P on the Y-axis versus time, what you would see is you would see an increase.

Now initially the increase would be greater because you have more of A. Overtime what will happen is the concentration of A will decrease because now A is getting converted to P, correct? So as the concentration of A decreases, the rate of formation of P over time will also decrease. So what you see is whenever you have graphs like this, you have this part which corresponds to what is called as the initial kinetics and slowly you reach a point where there is not much change.

So, studying the initial kinetics is very very important because it gives you lot of information about how the reaction changes with respect to the reactant or the product. So if I were to plot a similar graph where I show the change in concentration of the reactant, can you go ahead and plot it? So you can plot it on a similar graph where on the Y-axis you have concentration of A and on the X-axis you have time. So here what you would see is at time 0, you would have a large concentration of A, and over time, it will decrease because your reactant is actually decreasing over time.

Now the rate can be written in terms of formation of or in terms of consumption of A. So mathematically, it can be written as or it can be written as formation of P. Now as you see from this graph, the rate is directly proportional to the concentration of the starting material. So initially when you have starting material which is A, initially when you have more of A, the rate is faster, so dP/dt is essentially change of product versus time. So, you see that in initial kinetics, it goes faster.

So this is and it is given by usually, the proportionality constant is your rate constant. So if I were to plot dP/dt versus A, what would the plot look like. So I have kept an empty graph for you, so I am plotting dP/dt by A. So the plot would be a straight line since it is linearly correlating with A. Now certain terminology, if you have a single molecule involved in the transition state, it is called a unimolecular reaction. So, an elementary reaction if you have two molecules it would be called a bimolecular reaction.

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So now let us look at a hypothetical reaction. So, the hypothetical reaction would be A+B+C going to P. So now the rate of the reaction need not always linearly depend on the reactant. Let us say we do an experiment, where we measure how the concentration of the product or the rate changes with the concentration of the reactant. So, when I do this experiment, I do it with A, B and C and let us say what we get is that you have this is the change in terms of concentration of A, this is for concentration of B, and this is for concentration of C.

So, what do you observe here, here you observe a linear correlation like we saw earlier. So what you can say is that dP/dt is directly proportional to B. So here it is directly proportional to B. In the case of A, what you see is, the rate is initially less and then it increases. So, in this case, the rate let us say is proportional to concentration of A square. So here if you had on the X-axis square of the reactant concentration you would have gotten a straight line. But here since you have reactant concentration, initially you have a slower rate and it increases.

And in the third case you see is there is no dependence. So, if I were to combine all of these to write the expression for this particular reaction, what you would see is the rate would be equal to this expression. This is called as a rate law where you correlate the rate with the concentration of the reactants and usually you would see a k observed, which is a rate constant which you experimentally measure when you try to figure out the kinetics for this reaction.

So here what you say is the reaction is second order with respect to A and first order with respect to B and zeroth order with respect to C and you can also write what is called as the overall order which in this case would be 2+1 which is 3. So the overall order of this reaction is 3. Now what you need to understand is the order is different from the unimolecular, bimolecular, the molecularity that we were talking about. So, the overall order is the sum of the reactant orders.

So, in this case the overall order is 3. The molecularity is the number of molecules in the transition state of an elementary reaction. So, in this case we do not know if it is an elementary reaction that is all the reactants are coming at one point, the only thing we know is the overall order is 3. In the case where you have a single step reaction the number of molecules in the transition state corresponds to the molecularity.

So make sure you do not confuse this with the order of a reaction. The order need not be for an elementary reaction. So now that you have some idea about the reaction kinetics, what we will be doing in the next lecture is we will be looking at how to derive rate laws for more complex reactions.

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So, to get you thinking let us consider a very simple reaction A+B going to P. So, what we will be doing in the next class is we would be deriving the rate laws for the elementary reaction and various complex reactions which represent a simple transformation of A+B going to P. So, one example I have given here is A could possibly go to an intermediate I which could react with B and then give P. But we will look at this in detail in the next class. Thank you.