Mechanisms in Organic Chemistry
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Lecture - 10
Deriving the Rate Laws

So welcome to week 3 of reaction mechanisms. We will just summarize what we did in the last week.

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So in week 2, we looked at reaction coordinate diagrams. So what we had looked at is, first of all how to represent reactions as reaction coordinate diagrams and what these reaction coordinate diagrams mean and we had seen how the Y-axis gives us information about the stability of the reactants, the intermediates and also gives us information whether the reaction has a tendency to be in equilibrium and also tells us what the rate determining step is. We also looked at how what information we can get from the X-axis which is the reaction coordinate.

The reaction coordinate corresponds to the geometry of the compound, so it tells you information about the nature of the transition state and we had looked at the Hammond postulate to say whether the reaction, whether the transition state resembles the reactant or the product or intermediate. We had also looked at certain implications and how we can control reactions. So one, one example we had seen was of kinetic and thermodynamic control. So this is where you have a reactant R which can give you a product A or a product B.

The product A has a higher activation energy but is more stable whereas product B is less stable and also has a lower activation energy. So B is formed faster but A is more stable. So, if you do the reaction under kinetic control where speed is important, B is the major product; if you do the reaction under thermodynamic control where stability is important, A is the major product. So, we had looked at examples of these and how you can predict or you can modulate a reaction so that you get kinetic control or thermodynamic control and we had also looked at the Curtin-Hammett principle.

So this Curtin-Hammett principle essentially tells you the ratio of products formed when you have two conformers A and B, so A and B are conformers which can interconvert relatively easily so that is why you have a small energy of interconversion. The product ratio that is P_A and P_B is dictated mainly by the activation energy difference for formation of P_A from A and P_B from B, so basically this energy difference. I will draw it out so that it is easier for you to see.

So Curtin-Hammett principle essentially tells you that larger this difference, greater is the selectivity and based on Curtin-Hammett principle this would be the major product. And towards the end of the week, we had just started looking at reaction kinetics. So, we had done an introduction to reaction kinetics because reaction coordinate diagrams do not give you much information about the speed at which the reaction is taking place.

So, for that you need to understand the concept of reaction kinetics and I just introduced you to the concept of the order of a reaction and what a rate law means. So, in today's lecture what we do is we would look at how we derive rate laws.

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So let us look at a reaction where A+B gives product. So we can measure the change of concentration of A over time experimentally, we can also experimentally measure say the change of concentration of B over time and there is a rate constant that can also be experimentally measured. That is why we call this k observed. Now one possibility is it is an elementary reaction. So from what you have studied in the previous class, what is an elementary reaction? A single step reaction.

So if it is an elementary reaction, it means that both A and B are coming together in a single step to give you the product Sort of like your S_N2 reaction where you have a single step concerted reaction. So when you have a concerted reaction and let us say so obviously since it is concerted, both molecules would be participating in the transition state. So, the rate law would be, the rate would be given by, so if the transition state is such that 1 molecule of A comes with 1 molecule of B, you would see that the reaction would be first order in terms of A and B.

So this would be overall order would be to 2 where its first order in A and first order in B. Now in this case since it is an elementary reaction, the molecularity of the reaction is also 2. It is a bimolecular elementary reaction. So again, I want to emphasize that molecularity term is only used when you talk about elementary reaction and it corresponds to the number of molecules in the transition state. It is typically very difficult to get a termolecular reaction where you have 3 molecules coming together in a transition state, but it is not impossible.

There are examples where you have a termolecular transition state. It is just that it is not very common. So now we could derive the rate law quite easily for the elementary reaction. Now what do we do if the reaction is more complicated? It is deceptive when we are just mixing A and B and getting a product P, but when you actually write out the mechanism, it might be possible that A would be going to an intermediate I first and now the intermediate I is what reacts with B to give you P and so each of these processes will have their own rate constants.

So k_1 is the rate constant for the forward reaction going to I, k_{-1} it is the rate constant for the reverse reaction. So how do we actually derive the rate law for such complex reaction? So that is what we will do in this lecture. So when you write the rate law for a reaction like this, by definition the rate law is getting the relationship between the reactants, the rate constant and relating that to the rate. Now in this case you have multiple processes happening.

So to first write the rate, you always start with the product so the rate of formation of P would be dependent on the rate constant k_2, concentration of I and concentration of B. So you always start from the right, which is formation of the product. Now this is not the rate law because it does not take into account k_1, k_{-1} and concentration of A which is the other reactant. So, this is not your complete rate law. So what do we do in complex situations like this?

So simplification is what is known as a steady state approximation and remember the steady state approximation can be applied only to intermediates or transient and highly reactive species. So in this case you have the intermediate I. The steady state approximation essentially tells you that, after a point in the reaction, you have almost a steady concentration of I. That means as soon as I is formed, it is also consumed. So initially you have I being formed from A and as soon as it is formed, it is consumed to give you P or come back to A.

So this is what steady state mean, just like the English word you have a steady state of I. Mathematically what that would imply is that you essentially have rate of change of I would be equal to 0, right? So mathematically it means that after a point you have a steady state that means the rate of I does not change with time. As soon as it is formed it is consumed. So based on steady state approximation, the rate of change of I is 0. What that means is the rate at which I is formed is equal to the rate at which I is consumed.

Now let us look at mathematically how we can express both of these. So, what is, what is the process that leads to formation of I? I want you to think about it and write it in your books. If you want you can press the pause button. All right? Now what are the processes that lead to consumption of I, again I would like you to think about it, write it in your notebook and you can press the pause button if you want. All right? So what leads to formation of I? A going to I is what leads to formation of I and how do you mathematically represent this?

So the formation rate would be given by k_1 [A]. This is a basic application of whatever we had studied earlier. Right? when we had looked at just an elementary reaction. Now consumption, what are the processes, there are two process processes. One is I going back to A and that would be given by k_{-1} [I] and what is the second process, the second process is I interacting with B to give you the product. So the rate for that would be given by k_2 x [I] x [B]. Right? Because it is dependent on I and B.

So now let us go ahead and with this information, so we have now the information that dI/ dt is given by this. Steady state approximation means the rate of formation is equal to the rate of consumption. So applying steady state approximation, we will call it SSA. What you get is $k1[A]$ which is the rate of formation is equal to $k_{-}1[I] + k2[I]$ x [B]. So essentially what that means is if I were to write the intermediate I in terms of A and B, this would be, so now we are taking out I, so it would be, so in other words $k1[A]/k_{-1} + k2[B] = [I]$.

Now we can go ahead and put that in our original rate equation. So what you get is the rate = k_2 [I] x [B], so I will go ahead and write concentration of B and in terms of concentration of I, I would write $k1[A]$. So what you get would be the rate law for this complex reaction. So now we have expressed the rate in terms of the rate constants and the reactants, so you do not see the intermediate here, this is the rate law for this complex reaction shown here.

So we have applied the steady state approximation to get the relationship between the reactants and the rate constants. Now we will look at how to use these equations in understanding reaction mechanisms slightly later, but I hope you get now an idea of how you can apply the steady state approximation to derive Rate laws for complex reactions. Now let us consider another scenario. So I have given you one scenario of A+B going to P.

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Now you can also have another possibility where what you have is A and B react together to give you the intermediate I and then I gives you the product P. So let us try to derive the rate law for this process. So as I told you, you always start from the right, so initially the rate you start off. In this case it is k_2 x [I] because it is the intermediate that gives you P. Now we need to express I in terms of A and B, so again we will apply steady state approximation and what you get here would be, what are the things which lead to formation of I?

So this leads to formation of I, and what are the things which lead to consumption of I? So this is formation and this is consumption. So, based on this, you can say that $k1[A]\ [B]/k_{-1}+k_2$ would be = I. So the rate law for this would be k_2k_1, so we are substituting it in this equation. So this would be the rate law for this complex reaction. So as you see, there is a slight change in the equation depending on the pathway of the reaction.

So here you see the rate law is slightly different from what we had seen in the earlier case which is again different from the elementary reaction. But what you would notice here is that in your denominator you do not have any term corresponding to your concentration of B. So essentially you can simplify this further to make this $k_{observed}$ [A] x [B]. Now what you notice this is, this form is very similar to the elementary reaction

although the $k_{observed}$ here has multiple processes with k_1 k_2 k_{-1} and k_2 in the in the denominator, but experimentally it is very difficult to distinguish between these two because the rate laws have a very similar form. Now I would like you to derive the rate law for another possibility which I am showing you for the same reaction. So here you have the possibility of the reactant A going to intermediate I and a side product P_1 and the intermediate I then reacts with B to give you the product P_2.

So what I would like you to do is I would like you to derive the rate law for this above reaction sequence. So I would, now that you have seen how to derive the rate law, I would like you to press the pause button on your video and sit and derive the rate law. So let us start deriving the rate law together and you can check your answers for those of you who have it in your notebooks. As I said you always start with the last step. So, in this case you have rate = k_2 concentration of I concentration of B because P_2 is our final product.

Now we will go ahead and apply the steady state approximation. So by applying the steady state approximation, again on the left we can put the processes that lead to formation of I which would be k_1 x [A] and the processes that lead to the consumption of I so that would be, this is one process which is you have the intermediate and P_1 going back to A and then the second process which is, so now you can write concentration of I.

So now we will go ahead and substitute that in the rate equation so you have the rate = k_2[B], so we are talking about this equation and now for concentration of I, I would put k_1[A] k_{-1}[P] + k_2[B], so that is k_1k_2 [A][B] + k_2[B]. So this would be the rate law for the complex reaction that we have seen. So now what we saw is, for a simple transformation which is A+B going to P depending on the mechanism of the reaction, one can have multiple rate laws. So now what we need to think of is how are these actually useful in determining reaction mechanisms.

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So. I would like you to think about this particular question. Can reaction kinetics be used to determine reaction mechanisms? I would like you to think about it for 2 minutes. Now that we have done a lot of mathematical, simple mathematics, we looked at how a simple A+B going to P, we can have multiple scenarios and derive different rate laws for this. Now that we have this information, can you use reaction kinetics to determine reaction mechanism?

So I would like you to think about this question and write down the points in your book. You can go ahead and press the pause button. So, what you would see is from reaction kinetics, you can actually arrive at mechanisms. So one, as I said we looked at 3-4 different possibilities. I might not know what the mechanism is. So looking at the kinetics where I do the experiment, determine the kinetics, I can get an idea about the reaction mechanism and we will look at examples of this in the next lecture.

You can also evaluate multiple mechanisms. So I can write say 2 or 3 mechanisms for a particular reaction. Based on the mechanism, I can derive the rate law and doing the experiment, I can say whether mechanism 1 is correct, mechanism 2 is correct or mechanism 3 is correct. So, I would need to do a very systematic study where I write the mechanism, derive the rate law, and then do the experiment and a lot of times people also use kinetics to determine a better catalyst for a particular reaction.

Since we are not directly looking at this in our particular course, I will not be going into much detail about this third point. In the next lecture what we will do is we will look at how reaction kinetics can be used to determine the mechanisms. So, you can practice writing the rate laws whatever we had done in the previous class, you can practice doing that, so for A+B going to P, you can again write down the rate laws for each process that we saw. So thank you and I will see you in the next lecture.