Symmetry, Stereochemistry And Application
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Lecture No-43
Kinetics of Organic Reactions

Welcome back to the course entitled symmetry stereochemistry and applications. In the last few lectures we have discussed about stereoselectivity, stereospecificity and there we have discussed about diastereoselective reactions enantioselective reactions etcetera. And in that we have discussed a couple of rules how to predict the diastereo selectivity in carbonyl addition reactions. So, as you have understood that these reactions are not simple and these reactions undergo through several steps of mechanism and those several steps have different rates of reaction.

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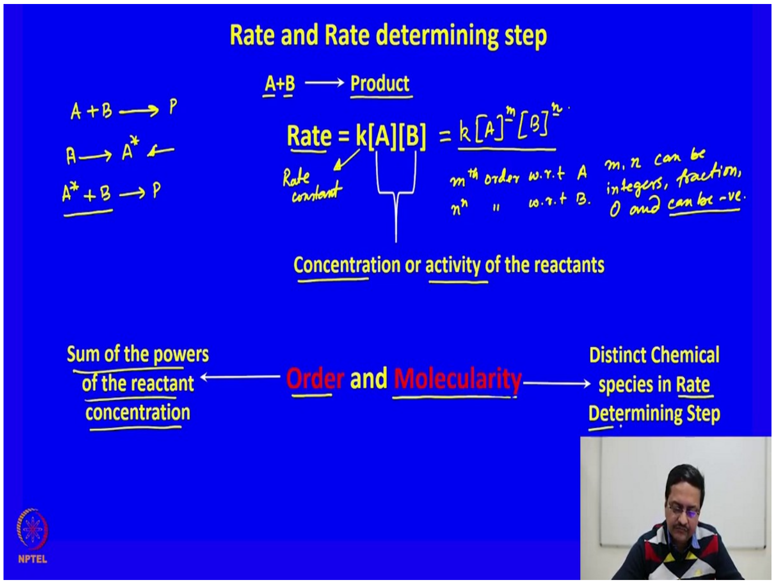

Rate and Rate determining step

$A + B \longrightarrow P$

$A \longrightarrow A^*$

$A^* + B \longrightarrow P$

$A+B \longrightarrow \text{Product}$

$\text{Rate} = k[A][B] = k[A]^m[B]^n$

Rate constant

m^{th} order w.r.t A

n^{n} " w.r.t B.

m, n can be integers, fraction, 0 and can be -ve.

Concentration or activity of the reactants

Sum of the powers of the reactant concentration ← Order and Molecularity → Distinct Chemical species in Rate Determining Step

So, one has to understand the kinetics of these organic reactions which are in general a very slow process. So, when we talk about the rates of reactions we try to identify how fast or how slow a particular reaction is proceeding or how fast the reaction takes place. So, when we when you talk about the rate of reaction suppose we have two substrates two compounds are added and we expect to form a product.

The rate of the reaction is written as a rate constant k and as a product of this rate constant with some concentration or activity of the reactants, sometimes this concentration or activity is also replaced with a power; a to the power m and b to the power n. So, some powers of the reactants on the concentration is added in various reactions those powers are called the order of a particular reaction. So, when you write reaction rate in this manner then we say that this reaction is mth order with respect to a and nth order with respect to b.

That means this m and n can be integers, fraction, can be zero and in some rare cases can be negative this happens in case of radical reactions using HBr. So, this reaction when we talk about the order of a reaction we are talking about those powers that are raised while writing the expression of a rate. The molecularity of a reaction is the number of molecules that are interacting in the rate determining step.

So, a particular chemical reaction suppose a plus b to p happens through several steps where a is energized to a star then this a star collides with b to form the product and this reaction may be the slowest step. So, this may be this is a step where two molecules are involved. So, those two molecules reacting in this step determines the molecularity of this reaction as a bimolecular process. Suppose if this reaction is the slowest step then the molecularity of this step is one.

So, then it is termed as unimolecular reaction and remember that bimolecular, unimolecular, trimolecular reactions have no relationship with the order of that particular reaction. The order comes from the rate equation, molecularity comes from the number of molecules that are involved in the rate determining step.

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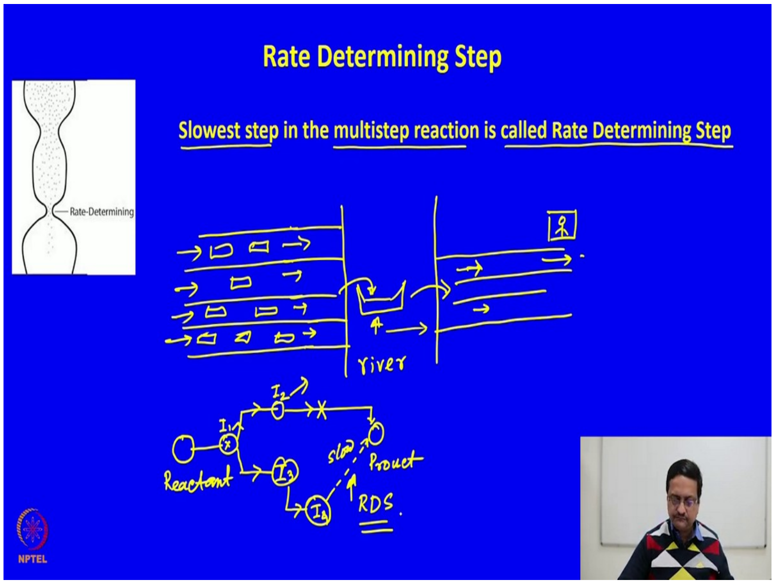

Rate Determining Step

Slowest step in the multistep reaction is called Rate Determining Step

Now you may be asking what does this rate determining step mean? The rate determining step of a chemical reaction in a multi step reaction is the slowest step of a particular reaction. We can give two examples, one example is suppose you have a large four lane highway and lots of cars are travelling at enormously large speed in this four lane highway and this four lane highway leads to a river bank.

So, in this river you have only one ship to carry these cars on it and transfer to the other side of the river and then on the other side of the river the road continues. So, now if you are an observer sitting here and trying to count the number of cars that are passing in front of you, this number of cars that are passing in front of you will be determined by this ship which is transferring the cars from one side to the other side of the river.

So, no matter how fast these cars were moving towards the river bank the number of cars that you would observe on the other side of the river is based on the speed at which this ship transfers the cars to the other side. So, this transferring of the cars from one side to other side by the ship is the slowest step and this determines the rate of your counting of cars on the other side of the river. So, this is the rate determining step.

So, similarly suppose you start with a reactant and you have to reach a product. So, in that path you have some intermediate I1 and then the reaction can follow a path which is through an intermediate I2 and it goes to the product it may be possible that it goes through a different route where you have an intermediate I3 which in turn forms a third intermediate I4 and then I4 to this product is slow what will happen is that this reaction will always tend to follow this path.

So, now by some means if we try to block this path by withdrawing this intermediate from the reaction medium and we try to force the reaction to proceed through this path to give the product then this rate of that reaction will be totally dependent on how fast this last step of conversion of I4 happens to the product and that will then be the rate determining step of that particular reaction. So, in a multi step process it becomes very important to identify the slowest step of a particular reaction.

And we need to try to improvise or you need to try to improve the rate of that particular reaction either by increasing the temperature or pressure or some other external factors.

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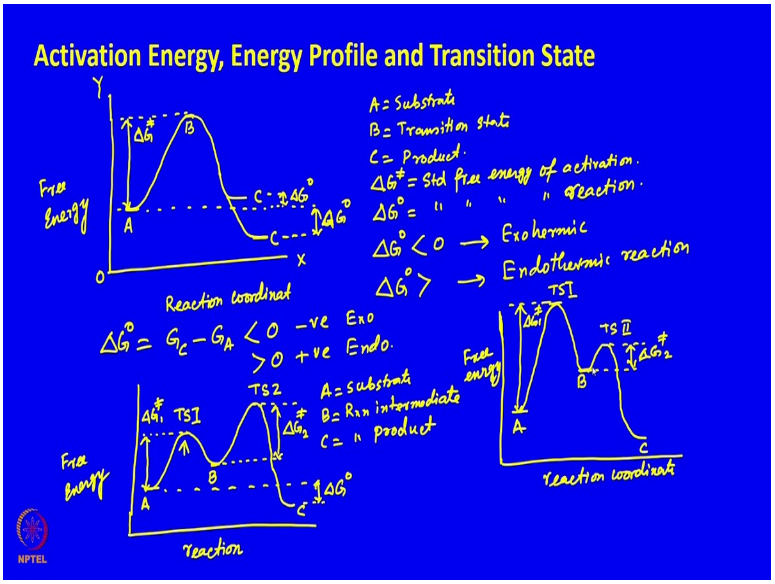

Activation Energy, Energy Profile and Transition State

A = Substrate
B = Transition state
C = Product.
$\Delta G^{\ddagger}$ = Std free energy of activation.
ΔG^{o} = " " " " reaction.
$\Delta G^{o} < 0 \rightarrow$ Exothermic
$\Delta G^{o} > \rightarrow$ Endothermic reaction

$\Delta G^{o} = G_C - G_A < 0$ −ve Exo
> 0 +ve Endo.

A = substrate
B = Rxn intermediate
C = " product

So, when we try to write the energy profile diagram of a chemical reaction which we have written very briefly when we discussed about SN1, SN2 and E1, E2 reaction. Let us try to understand that in more detail using the free energy versus reaction coordinate plot. So, here we plot free energy in the y axis and the progress of reaction which is called as reaction coordinate is plotted in the x axis.

Suppose we start with a particular free energy of the reactant as A and this goes through an activated transition state which is designated here as B and proceeds to form the product C which could be higher in free energy compared to A or could be lower in free energy compared to A. So, this reaction we have A equal to substrate, B is the transition state and C is the product. So, the difference in free energy between A and B is written as delta G hash and this is called the standard free energy of activation and the difference is called the standard free energy of the reaction.

Now this when the delta G^0 is negative that is less than 0 then we call this reaction as exothermic and delta G zero greater than one is called the endothermic reaction. So, here in this case when the energy of C is lower. So, normally this delta G zero is nothing but the G of C minus G of A, so, in case where the energy of C is lower. So, this is negative. So, that is called the exothermic reaction and when this is greater than, I should specify that greater than zero and less than zero that is negative and positive.

So this is exo, this is endothermic reaction we have also seen that some reactions are not going through one particular step rather it involves two steps in the reaction mechanism for example in case of SN1 or E1 reaction. So, in that case we need to know what would be the free energy diagram for the reaction. One type of free energy diagram can be like this where the substrate a is here it goes through a transition state to form a reaction intermediate B and then it goes through another transition state to form the product C.

So, here A is equal to substrate, B equal to reaction intermediate just like carbocation intermediate and C is the reaction product. So, here what we see is there are two different activation barriers one is for the formation of B from A. So we can identify that as delta G1 hash and the second activation barrier is here which is termed as delta G hash 2 and the delta G0 of the reaction is determined as usual by the difference in free energy of the reactant and the product.

So, this is one condition where this first barrier is smaller compared to the second barrier which essentially means that the reaction intermediate is a very stable reaction intermediate, the other condition that one can think of where the reaction intermediate is unstable, the scenario will be slightly different. So, in this case the activation energy barrier for the formation of A to B is large compared to the activation energy barrier for B to C is less.

So, now we have presented two different conditions, in one case the formation of A to B is fast because the activation energy barrier is lower and the second one has higher activation energy barrier whereas here the A to B the activation energy barrier is very high and other activation barrier is low. So, this reaction intermediate B is an unstable reaction intermediate.

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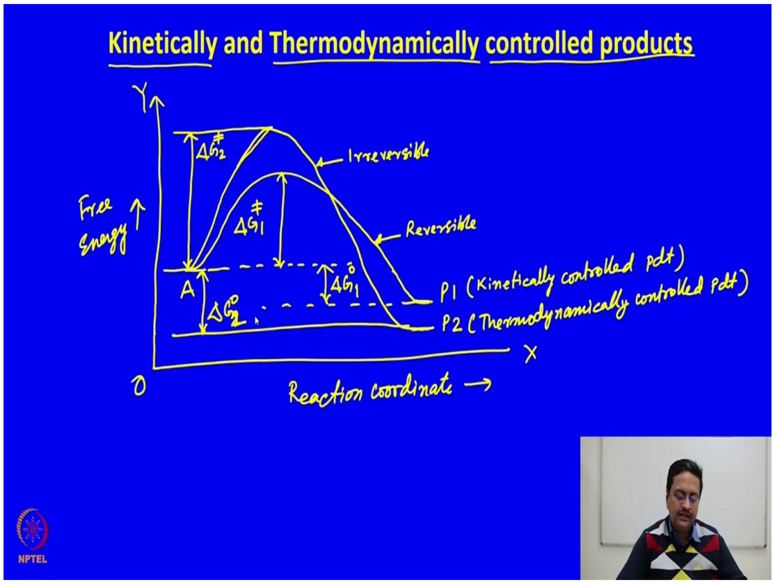

Kinetically and Thermodynamically controlled products

In many reactions what we see is that it is possible to form two different products in a given reaction and those two different products may be related by a thermodynamics and kinetics. So, we need to identify kinetically and thermodynamically controlled products in various reaction mechanisms. When we again draw free energy in y axis and reaction coordinate in x axis it may be possible that the reaction proceeds through a particular mechanism and gives rise to this product.

And it may be proceeding through a different reaction mechanism with much higher activation barrier and giving rise to a different product. So, if this reaction is reversible; and this reaction is irreversible then this product P1 is called the kinetically controlled product and this P2 is called the thermodynamically controlled product. The activation energy barrier for the thermodynamically controlled product is much larger while the activation barrier for the kinetically controlled product is much smaller.

And this thermodynamically controlled product has a delta G0 compared to the kinetically controlled product, delta G02 versus delta G01. So, these are the differences in reactions where you can end up getting two different products one may be going through a different reaction pathway. So, that the activation energy barrier is lower and the product that forms is a kinetically controlled product whereas a reaction that may be proceeding through a transition state of higher energy and end up giving you a lower energy thermodynamically stable product.

So, that is called a thermodynamically controlled product. So, I would like to request all of you to go through this from a standard textbook which is prescribed for this course to understand it in more detail. So, in the next week we will start discussing about various organic reactions like Diels Alder reaction, Wetting reactions, Pericyclic reactions etcetera, thank you.