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# Thermodynamic vs. Kinetic Control

## Transcript

00:00:00:24 - 00:00:15:92
**Dr.Jessie Key:** Well, again, Dr. Jessie Key here. In this slide show, we are going to examine the effect of temperature on the product distribution of electrophilic addition to a conjugated diene and introduce the concepts of thermodynamic and kinetic control.

00:00:18:48 - 00:00:52:28
**Dr.Jessie Key:** We saw earlier that hydrohalogenation of a simple symmetrical diene like buta-1,3-diene can yield two different products, the 1,2-adduct and the 1,4-adduct. However, the distribution of these products changes dramatically at different temperature. When this reaction is performed at zero degrees celsius, the 1,2-adduct is the major product with around 71% yield, and the 1,4-adduct is the minor product with about 29% yield.

00:00:52:84 - 00:01:27:93
**Dr.Jessie Key:** If instead the reaction is performed at higher temperature like 40 degrees Celsius, the 1,2-adduct is the minor product with about 15% yield, and the 1,4-adduct is the major product with about 85% yield. We can rationalize the effect of temperature on product distribution by examining an energy diagram for the reaction. Both products share the exact same first step proton transfer to generate the resonance-stabilized allylic carbocation.

00:01:27:93 - 00:02:03:19
**Dr.Jessie Key:** It is the nucleophilic attack step which differs with the 1,2-addition shown in green undergoing a lower activation energy and therefore a faster pathway to produce a higher energy 1,2-adduct product. While the 1,4-addition shown in pink has a higher activation energy, slower pathway that ends with a lower energy product. So there are two main differences here, the stability of the product and the activation energy of the nucleophilic attack.

00:02:03:26 - 00:02:35:40
**Dr.Jessie Key:** Focusing on the product energy, we see that the 1,4-adduct is lower energy than the 1,2-adduct because the resulting alkene is more substituted, being disubstituted. While focusing on the activation energy, the 1,2-addition occurs more rapidly with a lower

activation energy due to a proximity effect. After proton transfer occurs at carbon 1, the bromide nucleophile is much closer to the carbocation at carbon 2 compared to carbon 4.

00:02:35:40 - 00:02:54:01
**Dr.Jessie Key:** This facilitates the nucleophilic attack. We say that a reaction is under thermodynamic control when the ratio of products is determined by the product energy levels. At higher temperatures, there's sufficient energy to convert rapidly 1,2 and 1,4 products.

00:02:54:01 - 00:03:10:35
**Dr.Jessie Key:** So the determining factor is which product is the most stable. In the case of our addition products, it will be the product which has the most stabilized and therefore most substituted alkene. This is most often the 1,4 product.

00:03:10:39 - 00:03:36:34
**Dr.Jessie Key:** We call the most stable product the “Thermodynamic Product”. We say that a reaction is under kinetic control when the ratio of products is determined by the reaction rate. At low temperatures, there's not enough energy to interconvert 1,2 and 1,4-adducts frequently, and the product formed in majority will be the one that has the lowest activation energy.

00:03:36:34 - 00:03:51:54
**Dr.Jessie Key:** In the case of electrophilic addition to conjugated dienes, the kinetic product tends to be the 1,2-adduct due to the proximity effect. We call the product that is formed most quickly the “Kinetic Product”.