

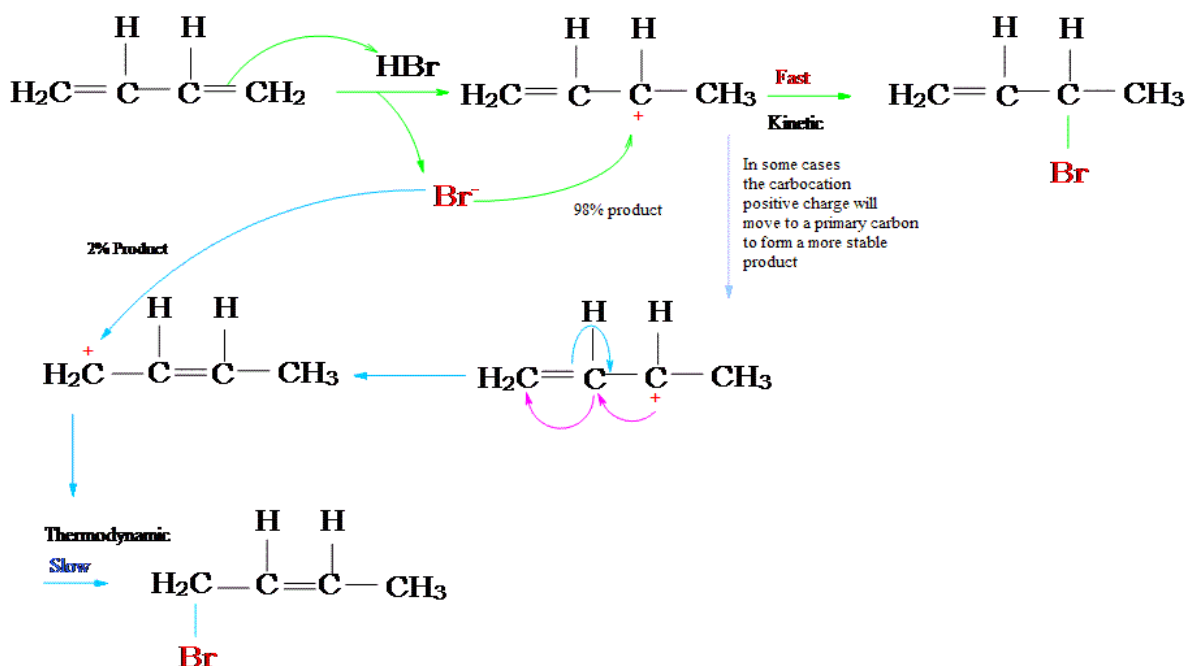
## 16.4: KINETIC VERSUS THERMODYNAMIC CONTROL

### THERMODYNAMIC VS KINETIC CONTROL

Upon electrophilic addition, the conjugated diene forms a mixture of two products—the kinetic product and the thermodynamic product—whose ratio is determined by the conditions of the reaction. A reaction yielding more thermodynamic product is under thermodynamic control, and likewise, a reaction that yields more kinetic product is under kinetic control. The reaction of one equivalent of hydrogen bromide with 1,3-butadiene gives different ratios of products under different reaction conditions to illustrate the difference between thermodynamic and kinetic control.

The green mechanism arrows show the formation of the kinetically favored 1,2-addition product. As shown in the reaction energy diagram below the reaction, the 1,2-addition reaction has a smaller activation energy and faster reaction rate. This faster reaction rate is what led to the term "kinetic control". This reaction is favored by low temperatures where the activation energy becomes the primary barrier to chemical reactivity.

The blue mechanism arrows show the formation of the 1,4-addition product, the thermodynamically favored product. As shown in the reaction energy diagram below the reaction, the product of the 1,4-addition reaction is lower in potential energy. Its formation is favored by reactions at high temperatures where there is adequate thermodynamic energy to overcome all of the activation energy barriers. This reaction is favored by elevated temperatures which led to the term "thermodynamic control".



Reaction Energy Diagram for 1,3-butadiene + HBr

The table below summarizes the empirically derived reactivity patterns for conjugated dienes at four different reaction conditions. Becoming familiar with the reactivity data and patterns in this table helps us build wisdom for determining the optimum reaction conditions when competing mechanisms are possible.

Table : Conjugated Dienes: Kinetic vs. Thermodynamic Conditions

Temperature	Kinetic or Thermodynamically Controlled	Speed of Reaction	1,2-adduct : 1,4-adduct Ratio
-15 °C	Kinetic	Fast	70:30
0 °C	Kinetic	Fast	60:40
40 °C	Thermodynamic	Slow	15:85
60 °C	Thermodynamic	Slow	10:90

A Warning: Not every reaction has different thermodynamic and kinetic products!

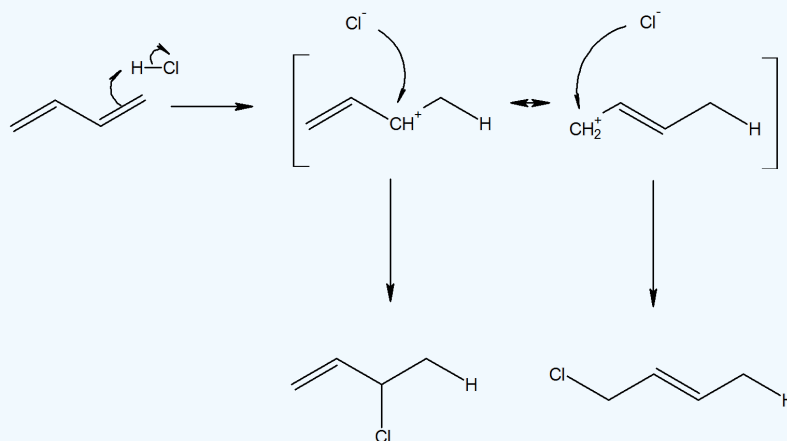
Note that not every reaction has an energy profile diagram like Figure 16.4.1, and not every reaction has different thermodynamic and kinetic products! If the transition states leading to the formation of C (e.g.,  $T_{C1}$ , and  $T_{C2}$ ) were to be higher in energy than that leading to B (e.g.,  $T_{B1}$ , and  $T_{B2}$ ), then B would simultaneously be both the thermodynamic and kinetic product. There are plenty of reactions in which the more stable product (*thermodynamic*) is also formed faster (*kinetic*).

### Exercise

5. Consider the reaction with 1,3-butadiene reacting with HCl. Propose a mechanism for the reaction.

**Answer**

5.



### CONTRIBUTORS AND ATTRIBUTIONS

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