# **Reaction Energy Diagrams**

### **1** Revisit Lewis Acid/Base Reactions

Example 1:

• this reaction "goes" from left to right because it gets 2 electrons into a bond, lowering their energy, the reaction is exothermic

#### Energy Diagram

Example 2:

• this reaction "goes" because although 1 bond is broken, 2 are formed

• the acid transfers a proton to the base, this is thus BOTH a Lewis and a Brønsted acid/base reaction

Energy Diagram

Energy 
$$\begin{array}{c} H & H \\ \circ C - C - H \\ H & H \end{array}$$
$$: \overset{\circ}{O}^{\circ} - t - Bu$$
$$\begin{array}{c} H & H \\ \vdots & H \end{array}$$

Reaction Coordinate

Example 3: not all acid/base reactions have to be exothermic:



• this reaction is fairly neutral as far as the energies of the electrons are concerned, however, it is driven by entropy (we will revisit entropy later...)

• this reaction is also a Brønsted acid/base reaction

Energy Diagram



Reaction Coordinate

Example 4:



• the products of this reaction are higher in energy than the reactants (the reaction is endothermic)

• nevertheless, we will see later that reactions such as these are important

Energy Diagram



Reaction Coordinate

## **2** Critical Connection Between Kinetics and Thermodynamics



• thus, a smaller Ea results in a larger k, i.e. a faster rate

• a larger Ea results in a smaller k, i.e. a slower rate



• the diagram shows the energy is of the ENTIRE SYSTEM (not just the alkene and fragments) as a function of progression along the "reaction coordinate"

• Each step (1 and 2) has its own energy barrier, Ea

• Ea(step 1) > Ea(step 2)

• step 1 is thus slower than step 2

• step 1 is the RATE DETERMINING STEP, i.e. the slowest step

• The value of the activation energy to make the first ionic intermediates is sufficiently large to result in a reaction that is not spontaneous, but is not too large that the reaction is precluded from happening

• So, this reaction "GOES" BOTH BECAUSE IT IS FAVORED THERMODYNAMICALLY AND BECAUSE IT IS NOT TOO SLOW KINETICALLY

• There are actually many reacti8ons that are favored thermodynamically that are too slow to go because of thermodynamics, which isn't always a bad thing!

Example, which of the following two reactions A or B is faster??



the rate determining step in A involves formation of a higher energy, less stable primary cation
the rate determining step in B involves formation of a lower energy, more stable tertiarty cation

Organic Reactions

• the rate determining step in B is faster than that in A, thus reaction B is overall faster than reaction A

#### The Hammond postulate:

all other things being equal (i.e. for similar or related reactions......

- More endothermic reactions have later, higher energy transition states (‡)
- More exothermic reactions have earlier, lower energy transition states (‡)

reaction coordinate

• The rate determining step, step 1, for reaction (A) is more endothermic than the same step for reaction (B)

- The more endothermic step has the LARGER Ea and the LATER transition state, Ea1(A) > Ea1(B)
- The more endothermic step also has a LATER transition state
- The first step in reaction A is SLOWER, because the intermediate cation is less stable
- The second step for reaction (A) is **more exothermic** than the second step for reaction (B)
- The more exothermic step has a SMALLER Ea, Ea2(A) < Ea2(B), and an earlier transition state
- The second step in reaction (A) is faster because the intermediate is less stable

• Reactions that FORM less stable intermediates are SLOWER, Reactions OF less stable intermediates are faster

Example Problem:



