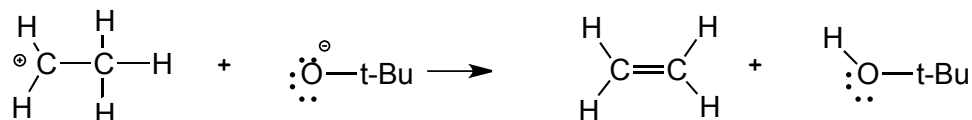


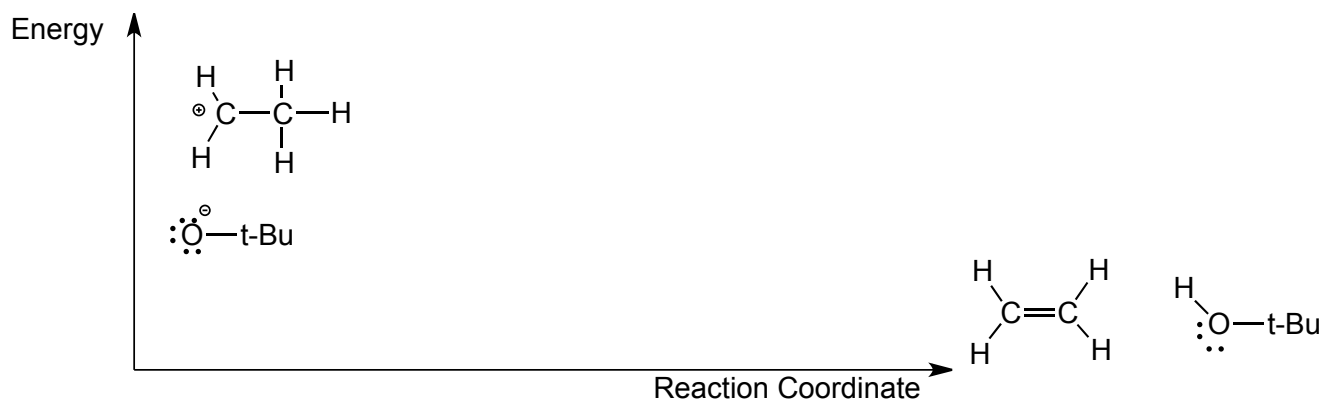
1 Revisit Lewis Acid/Base Reactions

Example 1:

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

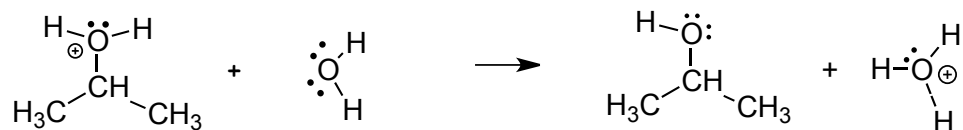
Energy DiagramExample 2:

- 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

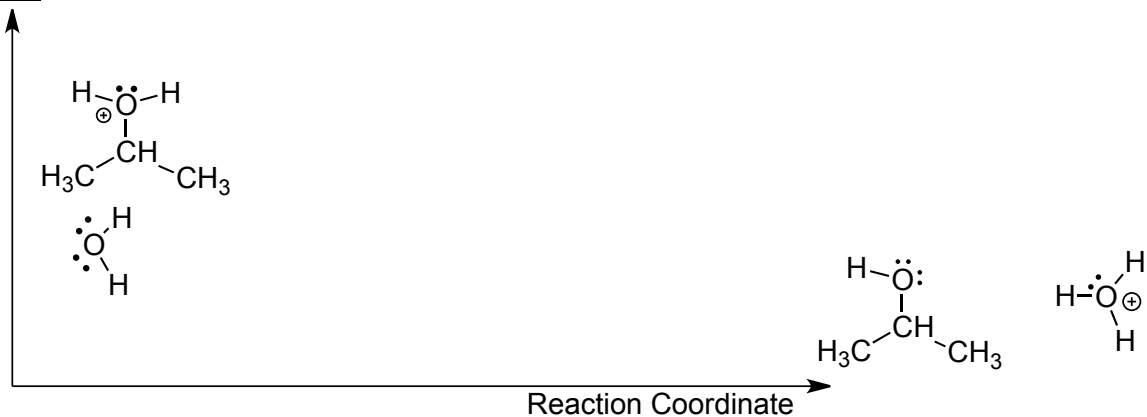
Example 3:

not all acid/base reactions have to be exothermic:

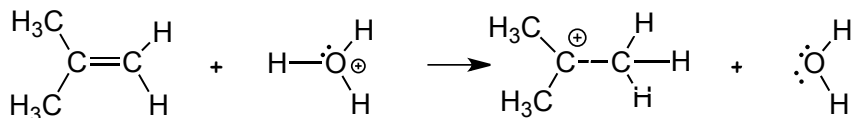


- this reaction is fairly neutral as far as the energies of the electrons are concerned, however, it is driven by entropy (we will revisit entropy later...)
- this reaction is also a Brønsted acid/base reaction

Energy Diagram

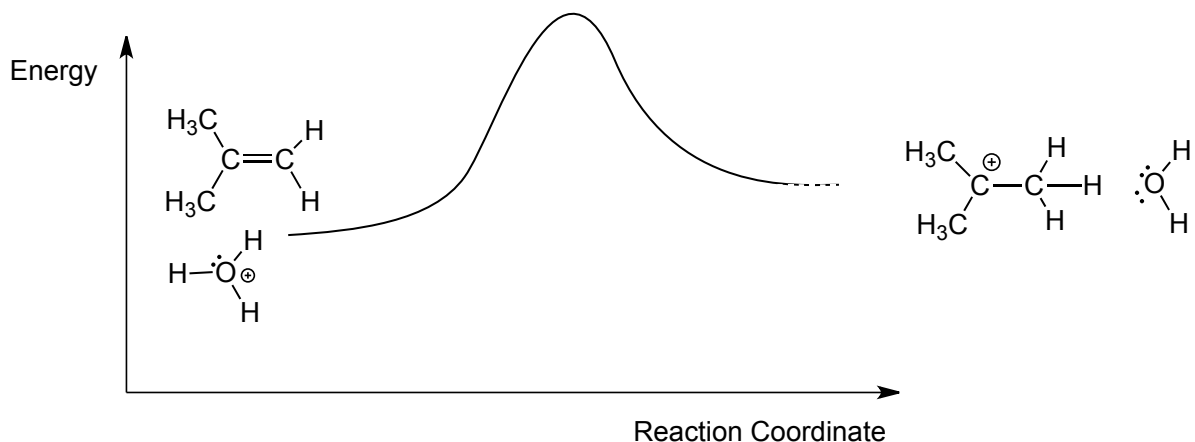


Example 4:



- 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**

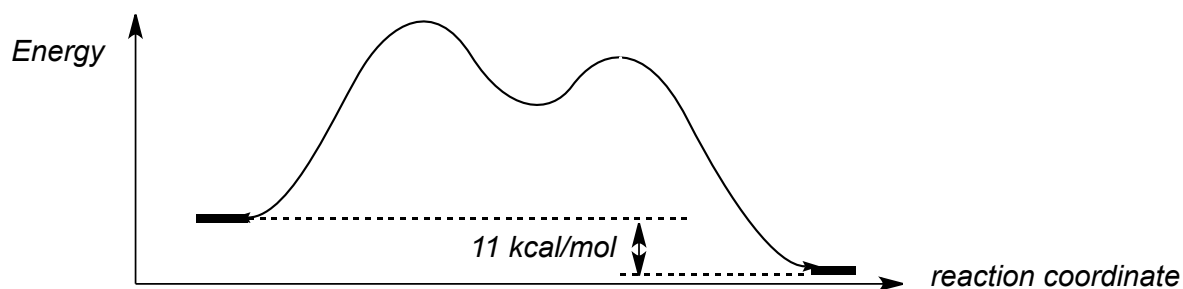
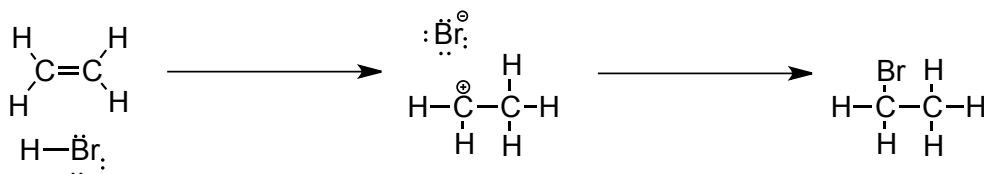
Energy Diagram



2 Critical Connection Between Kinetics and Thermodynamics

$$\text{rate} = k = A \exp(-E_a/RT)$$

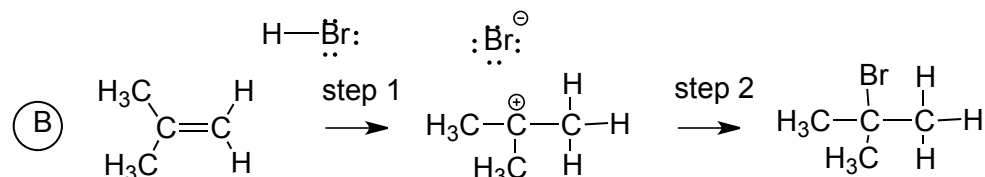
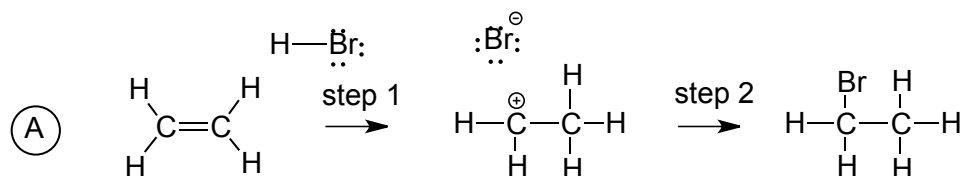
- thus, a **smaller E_a** results in a **larger k** , i.e. a **faster rate**
- a **larger E_a** results in a **smaller k** , i.e. a **slower rate**



• 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, E_a
- $E_a(\text{step 1}) > E_a(\text{step 2})$
- 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 reactions 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 tertiary cation

- 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** (\ddagger)
- More exothermic** reactions have **earlier, lower energy transition states** (\ddagger)



- 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 E_a and the LATER transition state, $E_{a1}(A) > E_{a1}(B)$
- 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 E_a , $E_{a2}(A) < E_{a2}(B)$, 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:

