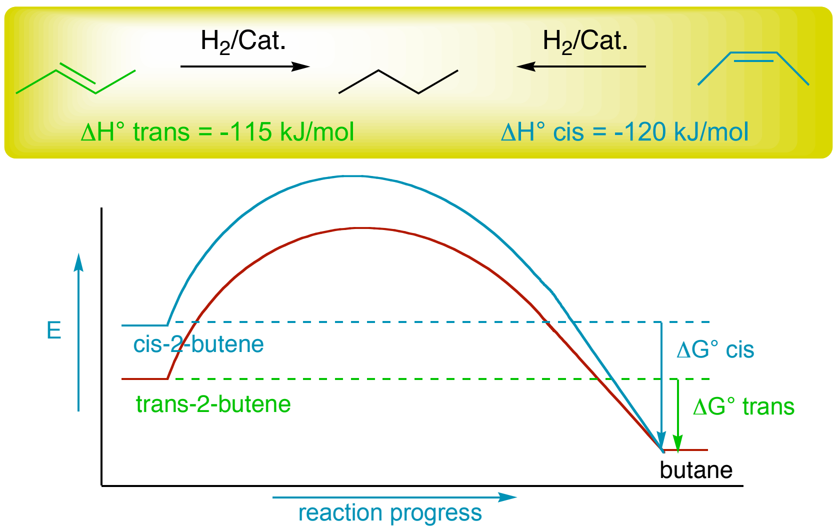
Chem 341

Lecture Summary 17
October 6, 2004

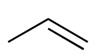
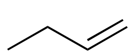
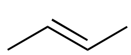
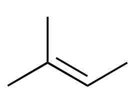
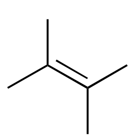
Chapter 6 - Alkenes: Structure and Reactivity

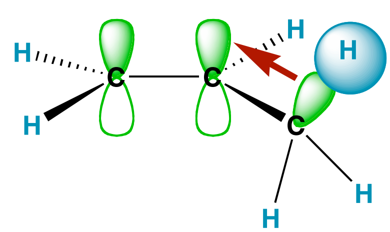
Alkene Stability

We saw last time that cis-alkenes are less stable than trans-alkenes due to steric crowding. This can be directly measured by measuring the heat of combustion or the heat of hydrogenation. These are useful techniques to compare the relative energies of molecules. Compare the heats of hydrogenation below. This is roughly equivalent to the difference in Gibbs Free Energy.



Alkenes that have more alkyl substituents also show greater stability of the pi-bond. Compare the heats of hydrogenation below for a series of substituted alkenes. The increase in stability (lowering of energy) with more alkyl groups is due to greater hyperconjugation from adjacent alkyl-H sigma bonds.

	ΔH° (hydrogenation)
	-137 kJ/mol
	-126 kJ/mol
	-126 kJ/mol
	-115 kJ/mol
	-113 kJ/mol
	-111 kJ/mol



Hyperconjugation - the C-H sigma bond adjacent to a pi-bond helps to stabilize it by aligning and overlapping with it. It is kind of like a delocalization of electrons, but not really a resonance situation. It is more like a very weak pi-bond. The more alkyl groups attached to the pi-bond, the more hyperconjugation exists. The same thing is seen with carbocations as they have an empty p-orbital that the attached alkyl groups donate into and stabilize.

Electrophilic Addition to Alkenes

We have discussed the reaction of HBr to ethane previously. This is called an electrophilic addition to an alkene because in the first step, a pi bond gets protonated by the electrophile (H^+). If the double bond is not symmetrically substituted then there exists the possibility of producing two different constitutional isomers. In fact, the reaction is REGIOSPECIFIC. In the example below, only the product with the Br attached to the more substituted 3° carbon is produced. Again, the more substituted carbocation is more stable. The reaction will proceed by the lowest energy pathway available.