



Chem 34I • Organic Chemistry I

Lecture Summary 13 • September 24, 2007

Chapter 5 - Overview of Organic Reactions

Polar Reactions

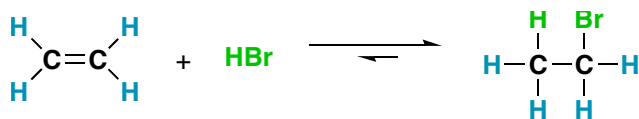
Most reactions occur through polar heterolytic bond breaking and making. They occur due to the attraction between positive and negatively charged parts of a molecule. Thus, it is important to remember how electronegative atoms influence the polarization of bonds. In any polar reaction there is an electron deficient species and an electron rich species. We have special terms to refer to their role in a reaction.

Nucleophile (loves the nucleus) - these are electron rich and seek out positive charges.

Electrophile (loves electrons) - these are electron deficient and are seeking electrons.

A nucleophile will attack (push its electron density or electron pair towards) an electrophile.

There are two aspects to all reactions. **Thermodynamics** relates to the energy difference between the starting materials and the products. This affects the overall energy of the system and the equilibrium but says nothing about how reactants get to products. The **kinetics** of a reaction deals with the pathway the reagents follow to get to the product and affect the rate of the reaction. Let us examine the addition reaction of HBr and ethane.



$$K_{\text{eq}} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{CH}_2\text{CH}_2][\text{HBr}]} = 7.5 \times 10^7$$

Thermodynamics

The equilibrium constant for the addition reaction above is very large which means the reaction lies far to the right. That indicates the products are more stable or much lower in energy than the starting materials. Note: *Reactions will proceed to the lower energy side (downhill)*.

We can talk about the total change in the energy of a reaction from one side to the other. This is defined as the **Gibb's Free Energy** and this is related to the Equilibrium Constant. Gibbs free energy is made up of energy from the bonds that are broken or formed in a reaction (**Enthalpy**) and the change in the freedom of movement of atoms (**Entropy**).

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

↑
Gibb's Free Energy
total change in energy
in the system from
reactants to products

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

↑
Enthalpy
"Heat of Reaction"
total change in the
bonding energies of a
reaction

Entropy

Amount of freedom (or disorder). Greater entropy means more freedom, less entropy means more restricted

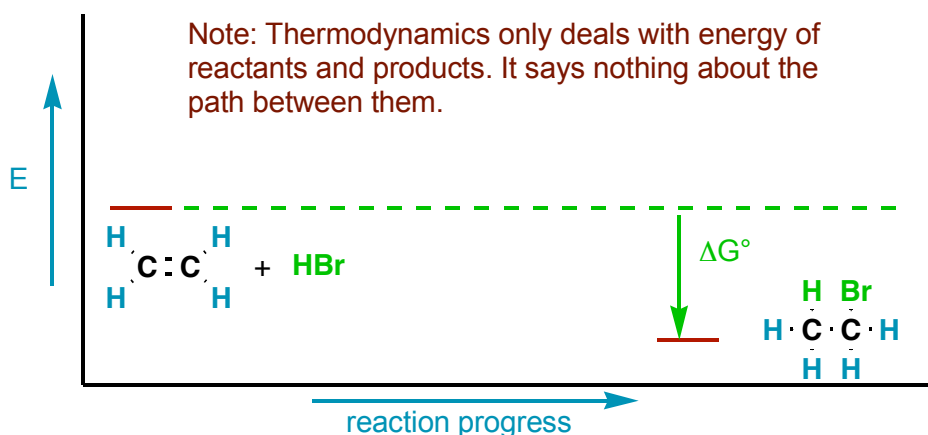
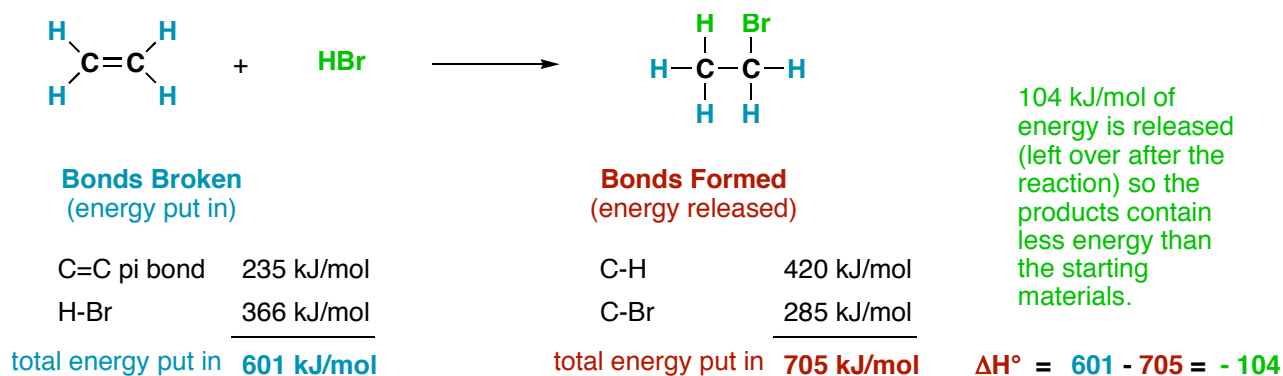
If ΔG° is negative (energy released) the reaction is downhill (exothermic).

ΔG° is positive (energy absorbed) the reaction is uphill (endothermic)

In many cases the entropy term is very small, so we can approximately determine whether a reaction will take place as written (exothermic) or not (endothermic) by looking at the total change in bonding energies. We can find that information tabulated from various information sources.

Bond Dissociation Energy - the energy required to homolytically break a bond.

Here is an example of how we can use BDE's to estimate the energy change in the addition of HBr to ethene.

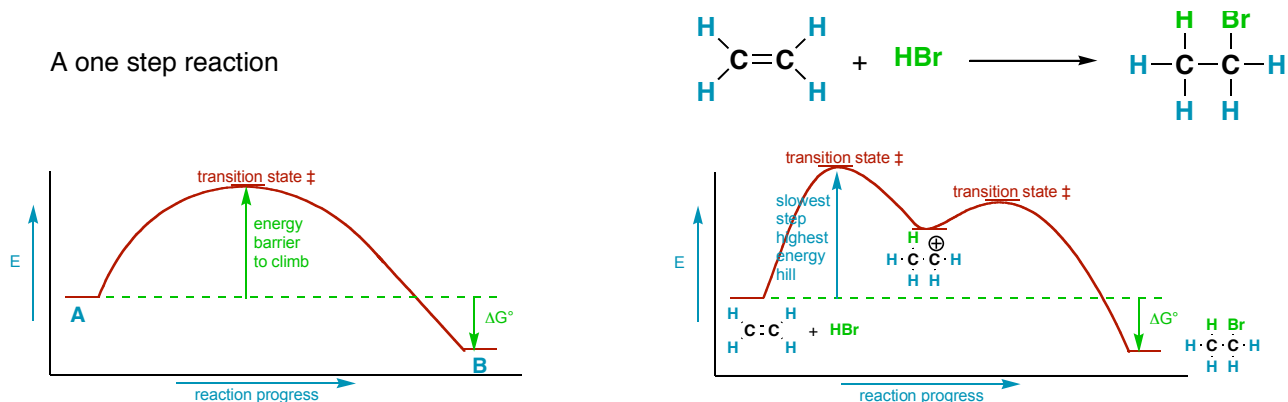


Kinetics

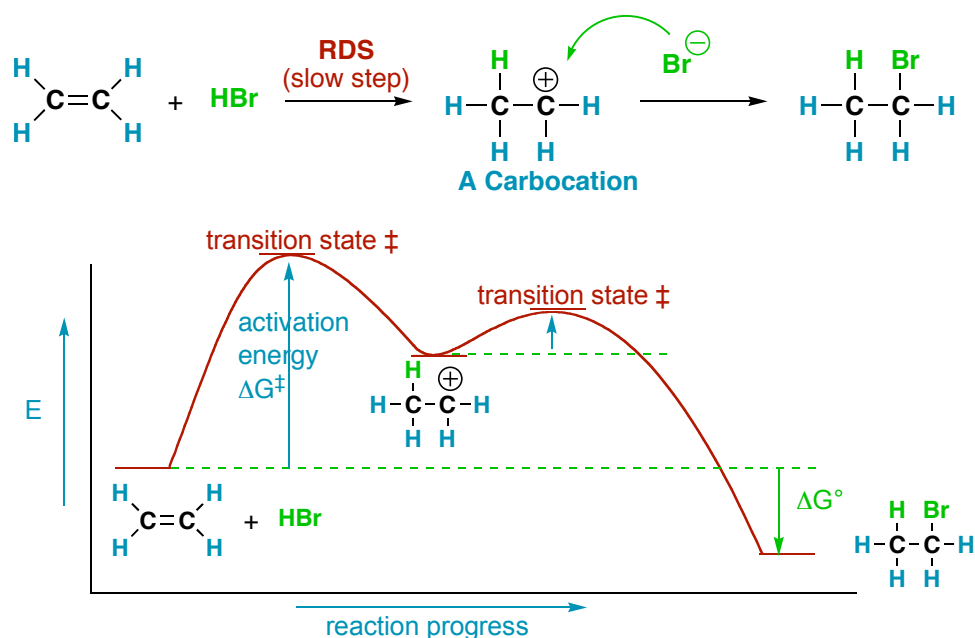
The position of equilibrium and the Gibb's free energy are only related to the relative energies of the starting materials and products. They say nothing about what pathway the molecules take to get from one side to the other. The path can be low and easy (a fast reaction) or it may need to climb very high in energy first (a slow reaction). In addition, the reaction may occur in several steps and pass through several different intermediate species. Chemists describe a reaction path graphically using a **Reaction Energy Diagram**. This is a plot of the total energy of the system (Y axis) as a function of the progress of the reaction (X axis).

Below are two reaction energy diagrams. The first is a general example of a one step reaction of reactants A converting to B. In order for the reaction to occur, the reagents need to rise in energy (as they come together or bonds change). The highest point of an energy barrier is

called the **transition state**. The structure of the molecules at the transition state does not exist for any length of time but immediately begin to fall toward the products (or back to the starting materials). The higher the energy barrier, the slower the reaction will take place (the more energy is required to get to the other side). The reaction diagram on the right shows the reaction of HBr addition to ethane. We will learn later in detail that this is a two step reaction. First a proton is transferred from HBr to the alkene forming a carbocation intermediate. This is seen as a plateau in the reaction diagram. It then climbs a little bit of an energy barrier to form the products. In the two step reaction, the first step has the highest energy barrier, so it is the slowest step. Note that the first step is endothermic (uphill in energy) while the second step is exothermic (downhill in energy).

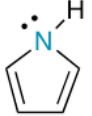
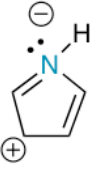
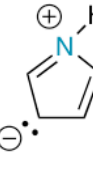
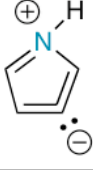


The reaction diagram below shows the reaction of HBr addition to ethane. First a proton is transferred from HBr to the alkene forming a carbocation intermediate. The slowest step in the reaction is called the **Rate Determining Step**. This would be the highest energy barrier in the reaction as it progresses from starting materials to products. In any given step of a reaction, there is an **Activation Energy** required to get over the hill. Simply stated, this is how much energy it takes to go over the highest point.



Note that this particular reaction has the highest activation energy in the first step. Other reactions could have the highest energy barrier in the second step. Indeed, other reactions could be much more complicated having multiple steps and multiple intermediates or even different pathways to different products.

Quiz of the day

<p>Which of the following structures is a valid resonance form for pyrrole?</p>  <p>pyrrole</p>	<input type="checkbox"/> 1:	
	<input checked="" type="checkbox"/> 2:	
	<input type="checkbox"/> 3:	
	<input type="checkbox"/> 4:	