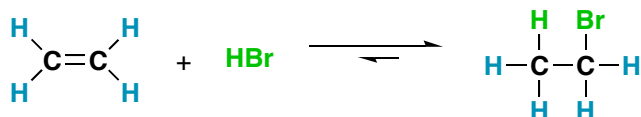


## Chapter 5 - Overview of Organic Reactions

## Polar Reactions

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

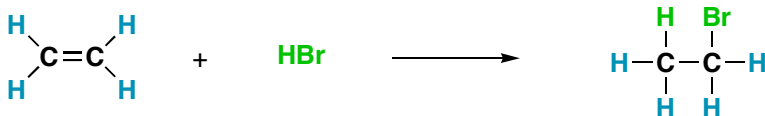
If  $\Delta G^\circ$  is negative (energy released) the reaction is downhill (exothermic).

$\Delta G^\circ$  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 ethane.



**Bonds Broken**  
(energy put in)

C=C pi bond	235 kJ/mol
H-Br	366 kJ/mol

total energy put in **601 kJ/mol**

**Bonds Formed**  
(energy released)

C-H	420 kJ/mol
C-Br	285 kJ/mol

total energy put in **705 kJ/mol**

104 kJ/mol of energy is released (left over after the reaction) so the products contain less energy than the starting materials.

$$\Delta H^\circ = 601 - 705 = -104$$

## 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 ethene. 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 exothermic (uphill in energy) while the second step is endothermic (downhill in energy).

A one step reaction

