

## The Study of Chemical Reactions

**Reading:** Wade chapter 4, sections 4-1- 4-12

**Study Problems:** 4-35, 4-36, 4-37, 4-38, 4-40, 4-43

### **Key Concepts and Skills:**

- Explain the mechanism and energetics of free-radical halogenation
- Calculate free energy changes from equilibrium constants, and calculate enthalpy changes from bond dissociation energies.
- Determine the order of a reaction, and use energy diagrams to discuss transition states, activation energies, intermediates, and the rate-determining step of a multistep reaction

### **Lecture Topics:**

#### **I. Aspects of Chemical Reactions**

The **mechanism** of a reaction is the step-by-step description of which bonds break and which bonds form (and in what order) in a reaction to give the observed products

**Thermodynamics** is the study of the energy changes accompanying chemical processes and allows us to compare the stability of reactants and products and predict which compounds are favored at equilibrium.

**Kinetics** is the study of reaction rates, and determines which products are formed fastest in a given reaction. Kinetics also allows us to predict how the rate will change if we change the reaction conditions.

Consider the chlorination of methane in the gas phase:



1. The reaction does not occur at room temperature in the absence of light
2. Blue light is absorbed by  $\text{Cl}_2$ , activating it so that it initiates the reaction with methane.
3. Many molecules of product are formed for every photon absorbed, that is, the reaction has a high “quantum yield”

These facts can be explained by the mechanism of the reaction, which is termed a free-radical chain reaction. This mechanism involves three main steps:

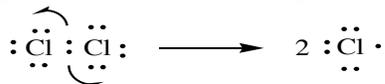
1. **Initiation** – generation of a reactive intermediate which is a free radical
2. **Propagation** – the reactive intermediate reacts with a stable molecule to form another reactive intermediate, and so on until the supply of reactants is exhausted or the reactive intermediate is destroyed.
3. **Termination** – side reactions that destroy the reactive intermediate tend to slow or stop the reaction.

#### **Further detail for chlorination of methane:**

**1. Initiation:** absorption of blue light by methane:



*Note:* the breaking of the Cl-Cl bond is a homolytic cleavage, that is, one electron of the pair that is in the bond goes to each chlorine atom. Half-arrows are used to denote this.



The Cl• species is a “radical”, containing a single unpaired electron. A radical has an odd number of valence electrons. It is electron deficient (no octet) and highly reactive.

Draw out examples of primary (1°), secondary (2°), and tertiary (3°) carbon radicals.

**2. Propagation:** The generation of free radicals from free radicals is characteristic of a propagation step; another reactive intermediate is produced, and the reaction can continue



**3. Termination:** combination of two free radicals consumes reactive intermediates, thus slowing or halting the reaction. Terminating steps consume free radicals without generating new ones. This usually occurs when the concentration of the reacting species is low, such as toward the end of the reaction.



## II. Energetics

**1. Thermodynamics-** consideration of the changes in enthalpy and entropy during a reaction allows us to predict the direction of spontaneity of a reaction.

Recall:  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$   $\mathbf{K_{eq}} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$

If  $K_{eq} > 1$ , products are favored; if  $K_{eq} < 1$  reactants are favored; if  $K_{eq} = 1$ , ~equal amounts of products and reactants formed at equilibrium.

Ex.:  $\text{CH}_4 + \text{Cl}_2 \rightleftharpoons \text{CH}_3\text{Cl} + \text{HCl}$   $K_{eq} = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]} = 1.1 \times 10^{19}$

When  $K_{eq} \gg 1$ , very little reactants are present at equilibrium. Recall:

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

where  $\Delta G$  is the Gibbs free energy change for the reaction – a measure of the amount of energy available to do work ( $\Delta G < 0$ ) or the amount of work that must be done ( $\Delta G > 0$ ) to make a reaction go in the desired direction

$\Delta G$  = free energy of products – free energy of the reactants.

If  $K_{eq} > 1$ ,  $\Delta G < 0$ , products are favored over (produced in greater amounts than) reactants at equilibrium.

If  $K_{eq} < 1$ ,  $\Delta G > 0$ , reactants are favored over (produced in greater amounts than) products at equilibrium

Intuitively, reactions should go from higher energy states to lower energy states; in general a reaction goes >99% to completion for  $\Delta G_{rxn}$  values more negative than  $-3.0$  kcal/mol.

Two factors contribute to changes in free energy: enthalpy and entropy, as designated in the equation:

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

$\Delta H$  = enthalpy of products - enthalpy of reactants

$\Delta S$  = entropy of products – entropy of reactants

•**Enthalpy** is the heat generated or absorbed by a reaction, and  $\Delta H$  is a measure of the relative strength of the bonds in the products and the reactants

Reactions tend to favor products with the lowest enthalpy (or the strongest bonds)

In an **exothermic** reaction,  $\Delta H < 0$ , heat is evolved, weaker bonds are broken and stronger bonds are formed.

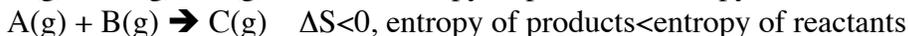
In an **endothermic** reaction,  $\Delta H > 0$ , heat is absorbed, and stronger bonds are broken, weaker bonds are formed.



The decrease in enthalpy makes a favorable contribution to  $\Delta G$

• **Entropy** is associated with randomness, disorder, and freedom of motion. Reactions tend to favor products with the greater entropy

Example:



A **positive** value of  $\Delta S$  makes a favorable contribution to  $\Delta G$ .

In most cases, enthalpy changes are much larger than entropy changes, and the enthalpy term dominates at ambient temperatures, thus a negative value of  $\Delta S$  doesn't necessarily doom a reaction.

Thus, the formation of strong bonds ( $\Delta H$ ) is usually the most important component in the driving force for a reaction



$\Delta G = -25 \text{ kcal/mol} - 0.86 \text{ kcal/mol} = -25.9 \text{ kcal/mol}$   
and  $\Delta G \approx \Delta H$

• **How can one predict whether a given reaction will be endo- or exothermic?**

Use a table (such as table 4-2 in text) of homolytic bond dissociation energies (BDE's):



BDE's are always positive, since energy must be input to break a bond!

$\Delta H_{\text{rxn}} = \Sigma(\text{BDE bonds broken}) - \Sigma(\text{BDE bonds formed})$

Example:



$\Delta H_{\text{rxn}} = (104 \text{ kcal/mol} + 58 \text{ kcal/mol}) - (84 \text{ kcal/mol} + 103 \text{ kcal/mol}) = -25 \text{ kcal/mol}$

This same process can be applied to the individual propagation steps in a mechanism; the sum of the enthalpies of both propagation steps gives the overall reaction enthalpy.

**2. Kinetics-** the study of reaction rates



Rate =  $k [\text{A}]^m [\text{B}]^n$

$k$  = rate constant

$m, n$  must be determined experimentally and cannot be deduced from a reaction's stoichiometry.

The rate equation depends on the mechanism of the reaction and on the rates of the individual steps in the mechanism.  $m$  is the order of the reaction with respect to A,  $n$  is the order of the reaction with respect to B. The overall order is  $m+n$ .

•**Activation energy**

$$k = Ae^{-E_a/RT}$$

$E_a$  is the activation energy, the minimum kinetic energy that molecules must have to undergo a successful collision leading to reaction. The term  $e^{-E_a/RT}$  is the fraction of collisions in which molecules have sufficient KE for reaction

A is a term dealing with the frequency of collisions and the fraction of collisions with the proper orientation for reaction to occur.

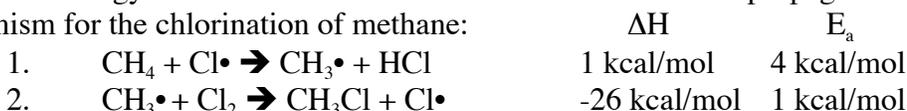
By looking at a Boltzmann distribution of kinetic energies of gas-phase molecules as a function of temperature, we find that at higher T's, a greater fraction of molecules have sufficient KE to result in reaction, and the reaction rate increases. Rate doubles for every 10°C rise in temperature..

•The **transition state** is the highest energy state in a molecular collision that leads to reaction. The activation energy represents the energy difference between reactants and the transition state. ( $E_a$  is always positive) Activation energy is an energy barrier that must be overcome in order for reaction to occur.

The transition state is transient and unstable and cannot be isolated → it is not an intermediate, which has some finite stability and lifetime.

•**Catalysts** do nothing to the energy of reactants and products, but rather create a transition state of lower energy to speed up reactions, so that more molecules have sufficient KE to surmount the energy barrier at a given temperature.

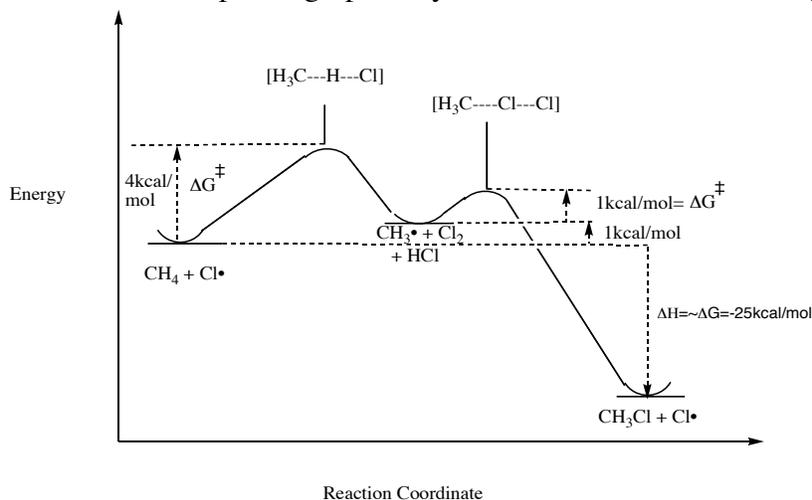
The **rate-limiting or rate-determining step** is the slowest step in a mechanism and has the highest energy barrier that must be surmounted. Consider the propagation steps of our mechanism for the chlorination of methane:



Clearly, the first step is rate-determining, since it has the highest energy barrier (4 kcal/mol) to surmount. The transition state for this step looks like:

$[H_3C\cdots H\cdots Cl]$ , with partial bonds between C, H, and Cl; ( $CH_3\cdot$  is an intermediate)

All this information can be depicted graphically on a reaction coordinate diagram:



Additional Problems for practice:

1. Draw a reaction energy diagram (graph of potential energy versus reaction coordinate) for a three-step endothermic reaction with the
  - (a) first step rate-determining
  - (b) the second step rate-determining
  - (c) the third step rate determining

Do the same (a-c) for a three step exothermic reaction. For each graph, indicate  $\Delta G$  for the reaction (is it positive or negative?). How many transition states are there? Label them.

2. Use the information in table 4-2 to calculate  $\Delta H^\circ$  for these reactions:
  - (a)  $\text{CH}_3\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{Br} + \text{H}_2\text{O}$
  - (b)  $\text{CH}_3\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{HBr}$
  - (c)  $\text{CH}_3\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{HI}$
  - (d)  $(\text{H}_3\text{C})_3\text{COH} + \text{HBr} \rightarrow (\text{H}_3\text{C})_3\text{CBr} + \text{H}_2\text{O}$
  - (e)  $(\text{H}_3\text{C})_2\text{CHOH} + \text{HCl} \rightarrow (\text{H}_3\text{C})_2\text{CHCl} + \text{H}_2\text{O}$

3. Draw the two possible conformations of *cis*-1,4-dimethylcyclohexane. Denote all 1,3-diaxial interactions for both conformations. Calculate the total strain energy for each conformation. Circle the more stable conformation. Finally, determine the ratio of the two conformations at equilibrium (use the relation between Gibbs free energy and the equilibrium constant). Repeat the exercise for *trans*-1,4-dimethylcyclohexane.