

CHEM 321 Organic Chemistry I - Professor Kathleen Kilway "Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 8 - 1, 2, 6, 7, 14, 17, 20, 21.

CHAPTER 8: EQUILIBRIA

Section 8.1

I. Preview

A- Vocabulary

- 1- **Transition state** is the top of an energy barrier, which separates energy minima.
- 2- **Oxonium ion** is a protonated alcohol.

Section 8.2

II. Equilibrium

A- Equilibrium Constant, K

- 1- **Equilibrium Constant** is related to the difference in energy between the starting materials and products.
 - a- If $K > 1$, then products are favored.
 - b- If $K < 1$, then the starting materials are more stable.
- 2- K is equal to the concentration of the products divided by the concentration of the reactants or starting materials.

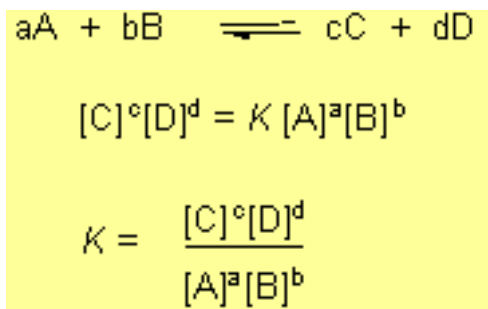


Figure 1

B- Gibbs Free Energy Change, ΔG°

- 1- **Gibbs free energy change** is the difference in energy between the starting materials and products in their standard states.

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -2.3RT \log K$$

where R is the gas constant (1.99×10^{-3} kcal/deg x mol), T is the absolute temperature.

- 2- **Enthalpy, ΔH°** , is the heat of reaction or a measure of the bond energy changes in a reaction.

- 3- **Entropy, ΔS°** , is the measure in change of order in the starting material and products.
- 4- Proper terms for free energy:
 - a- **Exergonic** is that the products are more stable than the reactants (i.e., $K > 1$).
 - b- **Endergonic** is that the reactants are more stable than the products (i.e., $K < 1$).
- 5- Equilibrium in % Products:

$$\Delta G^\circ = -2.3RT \log K$$

$$K = 10^{-\Delta G^\circ / 2.3RT}$$
 - a- For a 1 kcal/mol energy difference, reaction will go to 85% completion.
 - b- This energy analysis also holds for isomers and other product distributions.

C- Le Chatelier's Principle

- 1- This principle states that a system at equilibrium responds to stress in such a way so as to relieve the stress.
- 2- In a multistep reaction, where **A** reacts to form **B** (intermediate) which will react to form **C**. As long as there is some **B** present and there is enough energy to reach intermediate B, product **C** will be formed.

Section 8.3

III. Gibbs Standard Free Energy Change

A- ΔG°

- 1- ΔG° is composed of enthalpy (ΔH°) and entropy (ΔS°).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
- 2- ΔH°
 - a- It is related to the bond strengths in the starting materials and products.
 - b- It is possible to make accurate estimates using BDEs.
- 3- ΔS°
 - a- Entropy is related to freedom of movement.
 - b- The more restricted the molecule is, the more negative the entropy.
 - c- Entropy becomes more important with increasing temperature.

Section 8.4

IV. Rates of Chemical Reactions

A- The Rate is Dependent on Temperature and Concentration

B- Temperature Dependence - Boltzmann Distribution

- 1- The **Boltzmann Distribution** is the range of energies for a set of molecules at a given temperature.
- 2- If the temperature is increased, the average energy increases.
- 3- The reaction rate ~doubles for every 10 °C.

C- Concentration Dependence - Order of Reaction

- 1- **First-order reaction** is when rate for a reaction is dependent on the concentration of one species (S_{N1}).
- 2- **Second-order reaction** is when the rate for a reaction is dependent on the concentration of two species (S_{N2}).
- 3- **Pseudo-first-order reaction** is when the concentration of one of the reactants does not change during the reaction.

Section 8.5

V. Rate Constant

A- Rate Constant, k

- 1- k is the proportionality constant which is a fundamental property of any given chemical reaction.
- 2- It is in units of concentration per unit time.

B- Rate

- 1- **Rate** is how fast the concentrations of reactants change. It is dependent only on concentration of the reactants.
- 2- Whereas, the rate constant is how the rate will change as a function of reactant concentration. It varies with temperature, pressure, and solvent; but does not depend on concentrations.

Section 8.6

VI. Energy Barriers in Chemical Reactions: The Transition State and Activation Energy

A- Activation Energy, ΔG^\ddagger

- 1- It is the difference in free energy between the starting material and the transition state in a reaction.
- 2- This energy must be supplied in order for a reaction to occur.

B- S_{N2}

- 1- For the forward reaction:

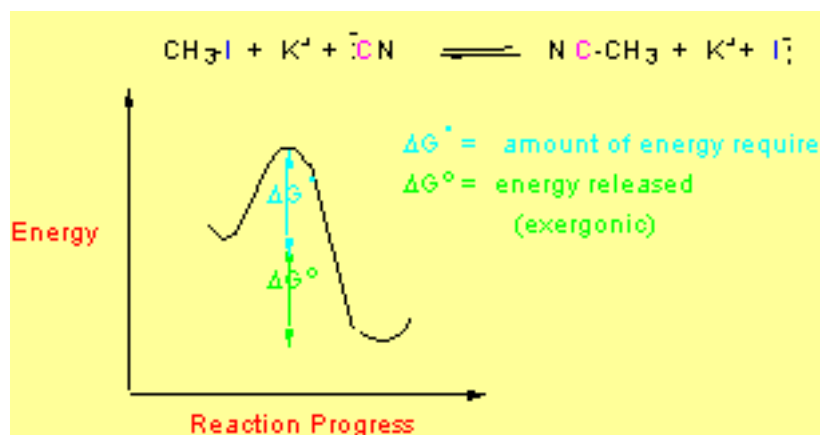


Figure 2

2- For the reverse reaction:

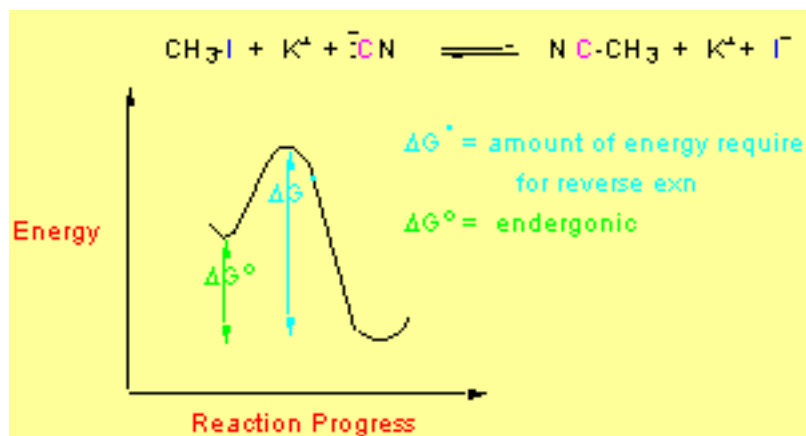


Figure 3

C- Microscopic Reversibility

- 1- If the mechanism of the forward reaction is known, then the mechanism of the reverse must also be known.

D- $\text{S}_{\text{N}}1$

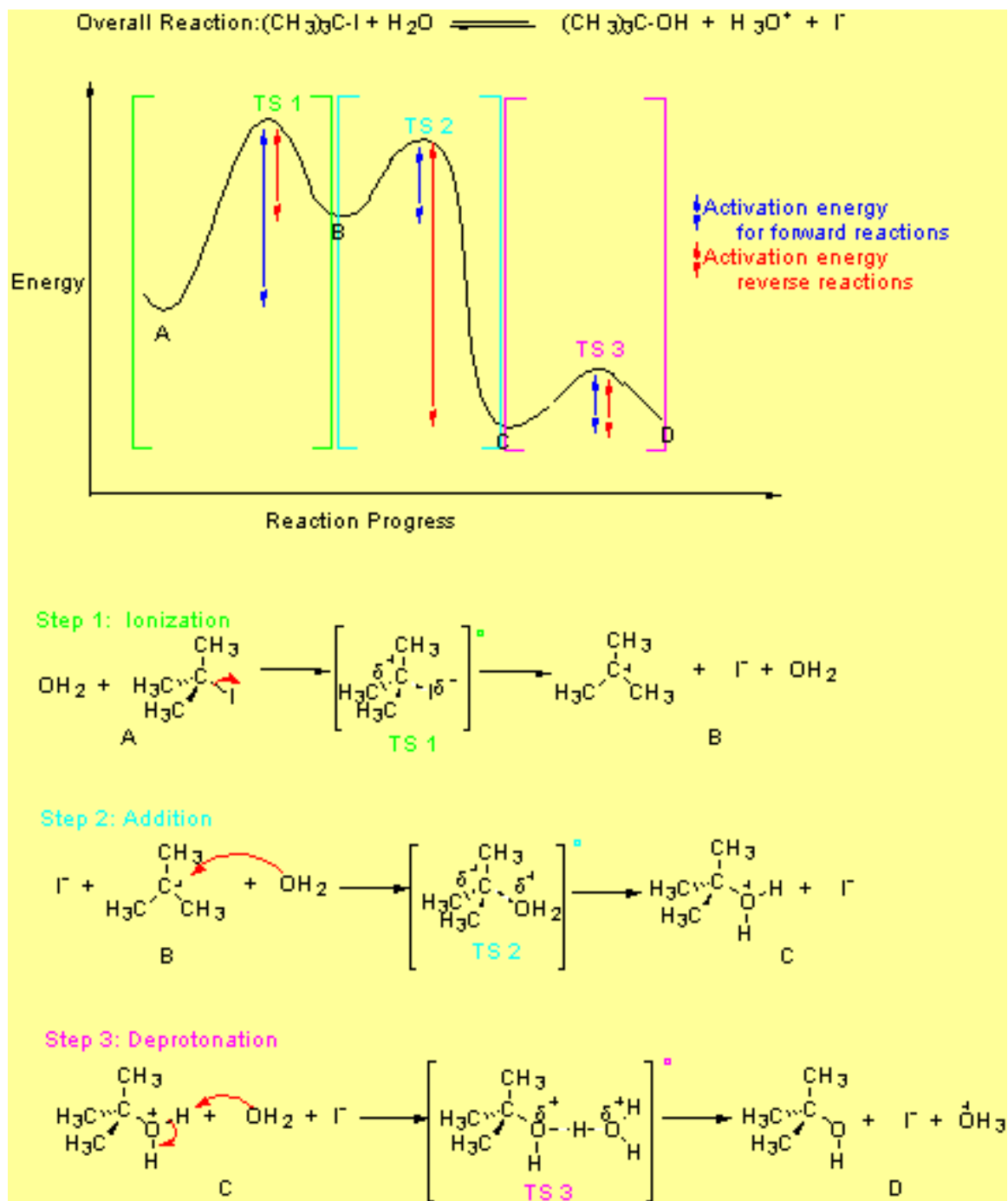


Figure 4

Section 8.7**VII. Reaction Mechanism****A- Rate Determining Step**

- 1- It is the slow step of the reaction.
- 2- For $\text{S}_{\text{N}}1$, it is the ionization step.

- 3- For steps faster than the rate determining step, it is not possible to measure their rate.

Section 8.8

VIII. The Hammond Postulate: Thermodynamics Versus Kinetics

A- Thermodynamics

- 1- **Thermodynamics** is the study of energy relationships.

B- Kinetics

- 1- This is the determination of the rates of reaction.

C- Thermodynamic Control

- 1- A **thermodynamically controlled** reaction is a reaction in which the product is determined by the relative energies of the products.

D- Kinetic Control

- 1- A **kinetically controlled** reaction is a reaction in which the product distribution is determined by the heights of the different transition states leading to products.

E- Hammond Postulate

- 1- The transition state for an endothermic reaction will resemble the product.
- 2- It can be equivalently stated as, "The transition state for an exothermic reaction will resemble the starting material."

Section 8.9

IX. Special Topic: Enzymes and Reaction Rates

A- Enzymes

- 1- **Enzymes** act as catalysts to lower the activation energy, thereby increasing reaction rates in biological systems, at a much lower heat than would be required in the laboratory.

Section 8.10

X. Summary

Equilibrium constant

Gibbs free energy

Thermodynamic vs. Kinetic Control

Activation Energy

Entropy

Enthalpy

Dependence of rate on temperature, pressure, and solvent

Transition States

Microscopic reversibility

Hammond Postulate