Organic Chemistry
Review of Thermodynamics and Kinetics

I. EQUILIBRIA IN ORGANIC REACTIONS (THERMODYNAMICS)

The equilibrium of a reaction describes how much of a particular reactant will be converted to product during the course of the reaction.

A. EQUILIBRIUM CONSTANT AND THE GIBBS FREE-ENERGY EQUATION

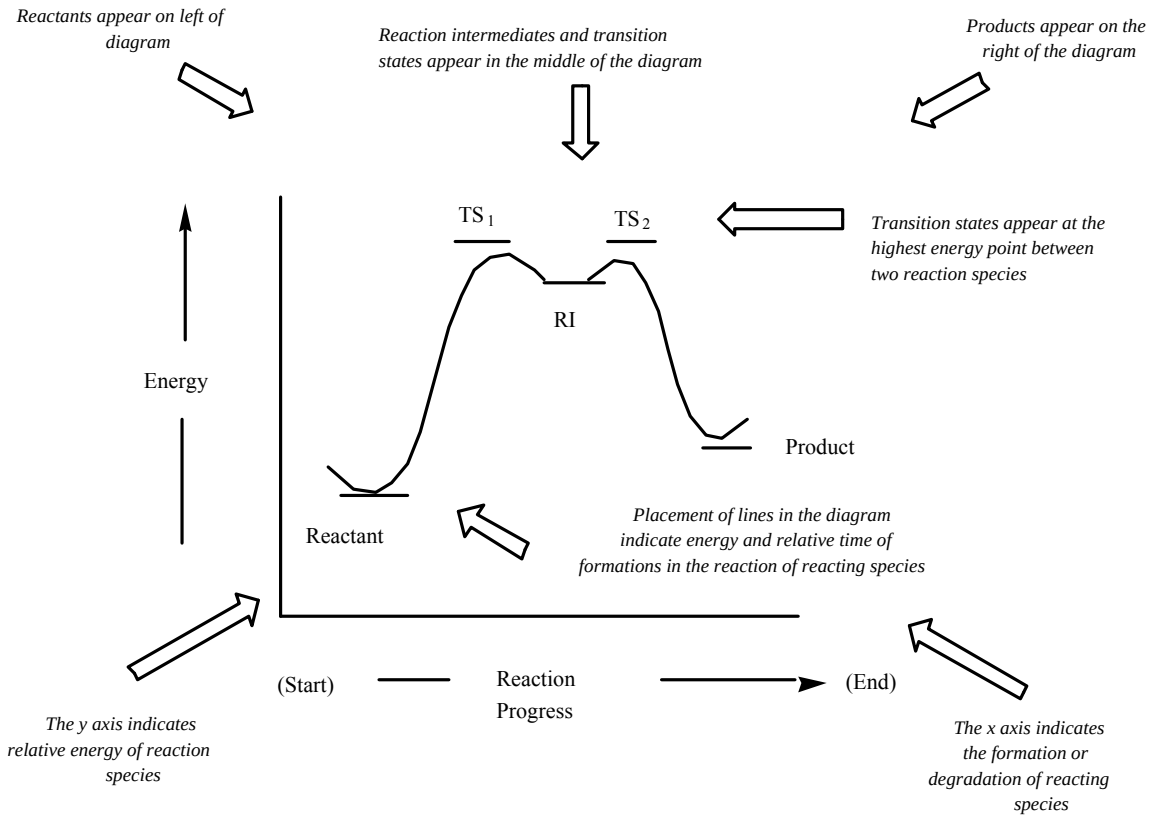
1. The equilibrium constant (K_{eq}) is the molar ratio of products over reactants.
2. The Gibbs Free Energy equation relates the equilibrium constant to the energy required for the reaction to occur.

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{or} \quad \Delta G° = -RT \ln K_{eq}$$

   a. ($\Delta H°$): The bond dissociation energy is the total energy required to homolytically break a bond into two radicals at 25°C in the gas phase.
   b. ($\Delta S°$): The entropy factor is the total disorder caused by a given reaction.

B. EQUILIBRIA AND REACTION ENERGY DIAGRAMS

1. A reaction energy diagram describes the relative energies of all species involved in a reaction and how that reaction proceeds.
2. The free-energy ($\Delta G°$) is the energy difference between reactants and products.
   a. A negative $\Delta G°$ indicates the products are more stable than the reactants (EXOTHERMIC REACTION).
   b. A positive $\Delta G°$ indicates the reactants are more stable than the products (ENDOTHERMIC REACTION).



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II. RATES OF ORGANIC REACTIONS (KINETICS)

The rate of an organic reaction describes how fast a particular reactant will be converted to a particular product.

A. RATE AND TRANSITION STATE ENERGIES

1. A transition state is a structure which represents the point of highest energy along the reaction pathway.
2. The activation energy ($\Delta G^{\pm}$) is the energy difference between the reactants and the transition state.
3. The rate of a given reaction is determined by the activation energy of the rate determining step of the reaction.
   a. A large activation energy results in a slow reaction.
   b. A small activation energy results in a fast reaction.

III. TRANSITION STATES AND REACTION INTERMEDIATES

A. A reaction intermediate is a species which results when some complete bond breaking and/or bond making has occurred. Although high in energy and often very unstable, reaction intermediates can be isolated in some cases.

B. A transition state is a species in which only partial bond making and/or breaking has occurred. Transition states can never be isolated.

IV. RELATIONSHIP BETWEEN EQUILIBRIA AND RATES OF REACTIONS (HAMMOND POSTULATE)

There is no absolute relationship between rate and equilibrium of a reaction however there is a postulate that relates these two quantities**.**

A. The HAMMOND POSTULATE states that the structure of the transition state can be inferred from the structure of a relatively stable species nearest in energy to the transition state along the reaction pathway.

1. The transition state will resemble the reactants in an exothermic reaction.
2. The transition state will resemble the products in an endothermic reaction.