

6.S: AN OVERVIEW OF ORGANIC REACTIONS (SUMMARY)

CONCEPTS & VOCABULARY

6.1: Kinds of Organic Reactions

- **Addition** reactions increase the number of sigma bonds in a molecule.
- **Elimination** reactions reduce the number of sigma bonds in a molecule.
- **Substitution** reactions incorporate replacement of an atom or group with another.
- **Rearrangement** reactions cause a molecule to be converted to a constitutional isomer without gaining or losing any atoms.

6.2: How Organic Reactions Occur: Mechanisms

- A reaction **mechanism** describes movement of electrons by using curved arrows to show bonds that are breaking and forming.
- **Homolysis** occurs when a bond breaks with each atom keeping one electron.
- **Heterolysis** occurs when a bond breaks and both electrons remain with one of the atoms.
- Some reactions occur in more than one step with a **reactive intermediate** formed briefly on the way to the new product.
- **Reactive intermediates** can be charged species such as carbocations and carbanions or uncharged species such as **radicals**.
- In organic chemistry Lewis acids are more often referred to as **electrophiles**, having an affinity for an electron pair.
- In organic chemistry Lewis bases are more often referred to as **nucleophiles**, having an electron pair that is available to bond to an **electrophile**.
- **Ionic** reactions involve charged species.
- **Polar** reactions involve bonds with unequally shared electrons.

6.3: Radical Reactions

- **Radical chain reactions** have three distinct phases: initiation, propagation and termination.
 - Initiation causes radicals to be created from non-radical species.
 - During the Propagation phase, radicals react with stable molecules to form new radicals.
 - Termination occurs when two radicals react together to form a stable molecule.

6.4: Polar Reactions

- Carbon when bonded to a halogen, oxygen, nitrogen, sulfur, or metal has a partial positive charge. This allows these carbons to react with many **nucleophiles**.
- For carbonyl groups bond polarity is reinforced by resonance making the carbon even more positive than in other molecules. This makes carbonyl groups prone to addition and substitution reactions with **nucleophiles**.
- **Nucleophiles** have electron rich atoms that are able to donate a pair of electrons.
- In nucleophilic substitution reactions, the **electrophile** is typically carbon bonded to a more electronegative atom.

6.5: An Example of a Polar Reaction: Addition of HBr to Ethylene

- Alkene addition reaction with HBr occurs through the pi bond reacting as a nucleophile and abstracting a proton from the acid. This creates a carbocation intermediate which reacts with the bromide ion to form the final product.
- Reaction rates for this alkene addition reaction increase with larger halogens and more substituted alkenes.
- Markovnikov's Rule states that addition reactions of unsymmetrical alkenes yield the more substituted product.

6.6: Using Curved Arrows in Polar Reaction Mechanisms

- Curved arrows in mechanism drawings always represent electrons moving, starting at either a bond or lone pair of electrons.
- Electrons flow from electron rich to electron poor.

6.7: Describing a Reaction: Equilibria, Rates, and Energy Changes

- **Exergonic reactions** have a negative free energy meaning they are thermodynamically favorable and give off energy.
- **Endergonic reactions** have a positive free energy and require energy from the surroundings to occur.

6.8: Describing a Reaction: Bond Dissociation Energies

- **Bond dissociation energy** for a molecule is the difference in enthalpy of formation (**homolytic**) for the products and reactants.
- **Bond dissociation energies** are independent of path of reaction, so they do not give direct information on mechanisms. However, they can be used to evaluate the results of individual steps of a mechanism.
- **Bond dissociation energies** show that sigma bonds formed with sp hybridized carbon are stronger than sp² which are stronger than bonds formed with sp³ carbons.
- **Bond dissociation energies** show that carbon-hydrogen bonds on primary carbons are stronger than secondary, which are stronger than tertiary.

6.9: Describing a Reaction: Energy Diagrams and Transition States

- **Reaction coordinate** diagrams are a special type of energy diagram that has the reaction coordinate (or reaction progress) on the x-axis.
- **Thermodynamics** of a reaction is conveyed on a reaction coordinate diagram by the difference in energy between the reactants and products.
- **Activation energy** is the energy barrier to a reaction occurring.
- A **transition state** is the highest energy point during the process of bonds forming and breaking in a reaction step.
- **Kinetics** of a reaction is conveyed on a **reaction coordinate** diagram by the difference in energy between the reactants and transition state.
- A **rate expression** relates rate to the **rate constant** and concentration of reactants.

6.10: Describing a Reaction: Intermediates

- A **reaction intermediate** is a short-lived species that goes on to react in a subsequent reaction step.
- **Reaction intermediates** appear as a local minimum (or valley) on a reaction coordinate diagram.
- **Catalysts** cause reaction rates to increase by lowering activation energy.

6.11: A Comparison between Biological Reactions and Laboratory Reactions

- An enzyme **active site** is the location where the enzyme interacts with its **substrate** and where **catalysis** occurs.
- **Substrates** are reactant molecules in enzymatic reactions.

SKILLS TO MASTER

- Skill 6.1 Identify organic reactions by type (addition, elimination, substitution, rearrangement).
- Skill 6.2 Draw homolytic and heterolytic bond breaking as part of reaction mechanisms.
- Skill 6.3 Identify radical and ionic reactions.
- Skill 6.4 Identify and write out steps in a typical radical substitution reaction (initiation, propagation, termination).
- Skill 6.5 Identify polarity of bonds in organic molecules.
- Skill 6.6 Use curved arrows to indicate movement of electrons in resonance and reaction mechanisms.
- Skill 6.7 Predict whether a chemical species will act as an electrophile or nucleophile.
- Skill 6.8 Write an equilibrium expression for a reaction.
- Skill 6.9 Determine the direction of a reaction based on the equilibrium constant.
- Skill 6.10 Explain how rate and equilibrium are related to ΔG° and K_{eq} .
- Skill 6.11 Calculate bond dissociation energy given enthalpies of formation for reactants and products.
- Skill 6.12 Describe order of bond strength based on bond dissociation energy.
- Skill 6.13 Explain activation energy, kinetics, thermodynamics and transition states based on energy diagrams (reaction coordinate diagrams).
- Skill 6.14 Predict possible transition state structures for single reaction steps.
- Skill 6.15 Differentiate between transition states and intermediates.
- Skill 6.16 Draw a reaction coordinate diagram for a given multi-step process.
- Skill 6.17 Interpret a reaction coordinate diagram for a multi-step process.
- Skill 6.18 Briefly explain how enzymes catalyze reactions.

MEMORIZATION TASKS

MT 6.1 Memorize that arrows in reaction mechanisms always define movement of electrons.

MT 6.2 Memorize the relative electronegativities of common atoms (necessary for determining polarity of bonds).

MT 6.3 Memorize the equations that relate equilibrium, free energy, enthalpy and entropy.

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

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

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