Lecture 9 Reaction Mechanisms, Chain Processes, and Biocatalysis

Goal of the lecture: To study the fundamental principles of reaction mechanisms, the nature of chain reactions, and the role of biocatalysts in accelerating and controlling chemical transformations.

Brief lecture notes: This lecture explores how chemical reactions occur at the molecular level by analyzing elementary reaction steps, intermediate species, and energy profiles. Students will learn to interpret reaction mechanisms, understand radical and chain processes, and recognize how enzymes act as highly efficient biological catalysts. The focus is placed on the relationship between molecular structure and reactivity, mechanistic pathways, and kinetic models used to describe multi-step and enzymatic reactions.

Main part

A reaction mechanism provides a detailed molecular description of the sequence of steps leading from reactants to products. Each step, called an elementary reaction, involves the collision of molecules or ions, forming intermediate species that often exist briefly.

For a general reaction:

$$aA + bB \rightarrow cC + dD$$

the mechanism might involve several steps such as:

1. $A + B \rightarrow AB^*$(formation of an activated complex)
2. $AB^* \rightarrow C + D$(decomposition to products)

Each step is characterized by its own rate constant and activation energy, determining how fast the overall process proceeds.

A potential energy diagram (Figure 1) typically illustrates how energy changes along the reaction coordinate, showing activation barriers and intermediate states.

Chain reactions are multi-step mechanisms involving reactive intermediates, often radicals, that propagate the reaction sequence. They consist of three main stages:

- Initiation: formation of radicals, e.g., through thermal or photochemical decomposition
- Propagation: radicals react with stable molecules to form new radicals, sustaining the reaction
- Termination: radicals combine to form stable molecules, ending the chain

Example — Chlorination of methane:

$$\mathrm{Cl_2} \xrightarrow{h\nu} 2\mathrm{Cl}\cdotp$$
$$\mathrm{Cl}\cdotp + \mathrm{CH_4} \rightarrow \mathrm{CH_3}\cdot + \mathrm{HCl}$$
$$\mathrm{CH_3}\cdot + \mathrm{Cl_2} \rightarrow \mathrm{CH_3Cl} + \mathrm{Cl}\cdotp$$

Here, each radical acts as a chain carrier, maintaining the reaction sequence. Chain reactions are fundamental in polymerization, combustion, and photochemical processes.

Biocatalysis and Enzyme Mechanisms

Biocatalysis involves the use of enzymes or whole cells to catalyze chemical reactions. Enzymes provide high specificity, selectivity, and efficiency under mild conditions. Their catalytic action is typically described by the Michaelis–Menten mechanism:

$$E + S \rightleftharpoons ES \rightarrow E + P$$

where E is the enzyme, S is the substrate, and P is the product. The corresponding rate equation is:

$$v = \frac{V_{max}[S]}{K_m + [S]}$$

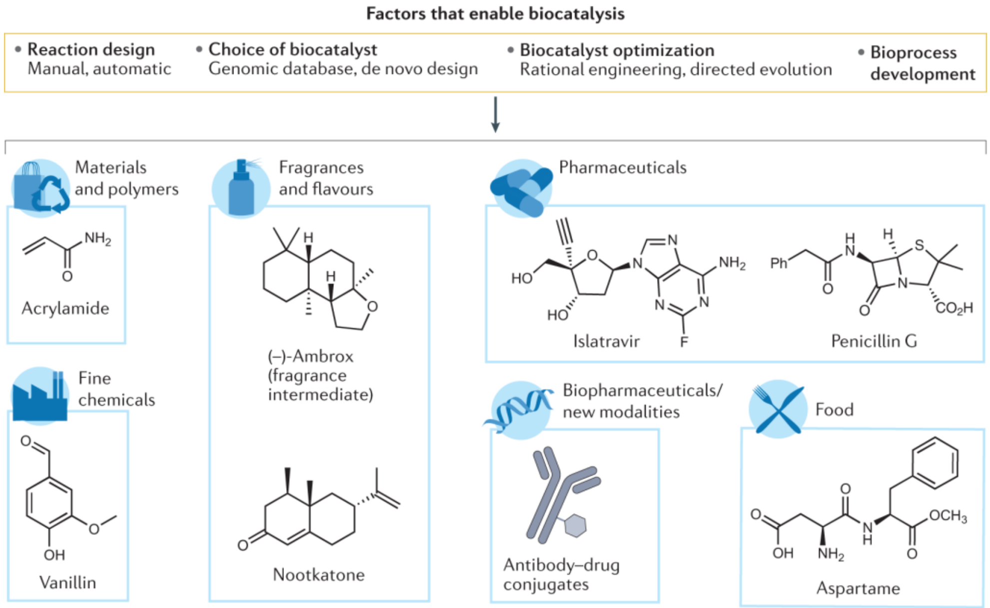
where V_{max} is the maximum rate and K_m the Michaelis constant, representing the affinity of the enzyme for the substrate.

Enzymes lower activation energy by stabilizing the transition state and orienting reactants precisely. Biocatalysis plays a crucial role in biochemical pathways, industrial biotechnology, and green chemistry, enabling sustainable and selective chemical production.

Comparative Characteristics

Type of Mechanism	Key Feature	Typical Example	Catalyst Type
Elementary Reaction	Single-step process	Gas-phase collision	None
Chain Reaction	Radical propagation	Hydrocarbon oxidation	Initiator (light, heat)
Enzymatic Reaction	Complex, selective mechanism	Hydrolysis, oxidation	Biological enzyme

Figure 1.



Questions for Self-Control

1. What distinguishes an elementary step from an overall chemical reaction?
2. Describe the main stages of a chain reaction and give an example.
3. How do enzymes lower the activation energy of biochemical reactions?
4. What is the significance of the Michaelis–Menten constant K_m?
5. How does temperature influence the rate of radical and enzymatic reactions differently?

Literature

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