Chapter 12 Part 4

Dr. Turner

Reaction Mechanisms

- A reaction mechanism is the process, or pathway, by which a reaction occurs
- For our purposes, we will consider a reaction mechanism to be the series of elementary reactions that composes an overall chemical reaction

Reaction Mechanisms

$$2\ O_3(g) \rightarrow 3\ O_2(g)$$

This is the overall reaction

Reaction Mechanisms

$$2\ O_3(g) \rightarrow 3\ O_2(g)$$

These are the two elementary reactions that make up the overall reaction

$$O_3(g) \rightarrow O_2(g) + O$$

$$O + O_3(g) \rightarrow 2O_2$$

Reaction Mechanisms

$$2\ O_3(g) \rightarrow 3\ O_2(g)$$

$$O_3(g) \rightarrow O_2(g) + O$$

$$O + O_3(g) \rightarrow 2O_2$$

The oxygen atom is made in one step, but consumed by the end of the reaction and is thus an intermediate

Reaction Mechanisms

$$2\,O_3(g) \rightarrow 3\,O_2(g)$$

$$O_3(g) \rightarrow O_2(g) + \cancel{O}$$

$$+\quad \cancel{O} + O_3(g) \rightarrow 2O_2$$

$$2\,O_3(g) \rightarrow 3\,O_2(g)$$

Since the oxygen atom intermediate is made in one elementary reaction but consumed in another, it does not appear in the overall reaction

Combining the two elementary reactions gives the overall reaction

Molecularity

- The molecularity of a reaction is the number of moles of reactant species (atoms, molecules, or ions).

Molecularity

- The molecularity of a reaction is the number of moles of reactant species (atoms, molecules, or ions).

Unimolecular Elementary Reactions	Bimolecular Elementary Reactions	Termolecular Elementary Reactions
$A \rightarrow$ products	$A + B \rightarrow$ products	$A + B + C \rightarrow$ products
	$2A \rightarrow$ products	$2A + B \rightarrow$ products
		$3A \rightarrow$ products

Elementary Reactions and Rate Laws

- Rate laws may not be derived from overall chemical reactions
- However, rate laws may be derived from elementary reactions

For an elementary reaction:

$$m[\mathrm{A}] + n[\mathrm{B}] + p[\mathrm{C}] + \cdots \rightarrow \text{products}$$

The rate law is:

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^p \cdots$$

Unimolecular Elementary Reactions

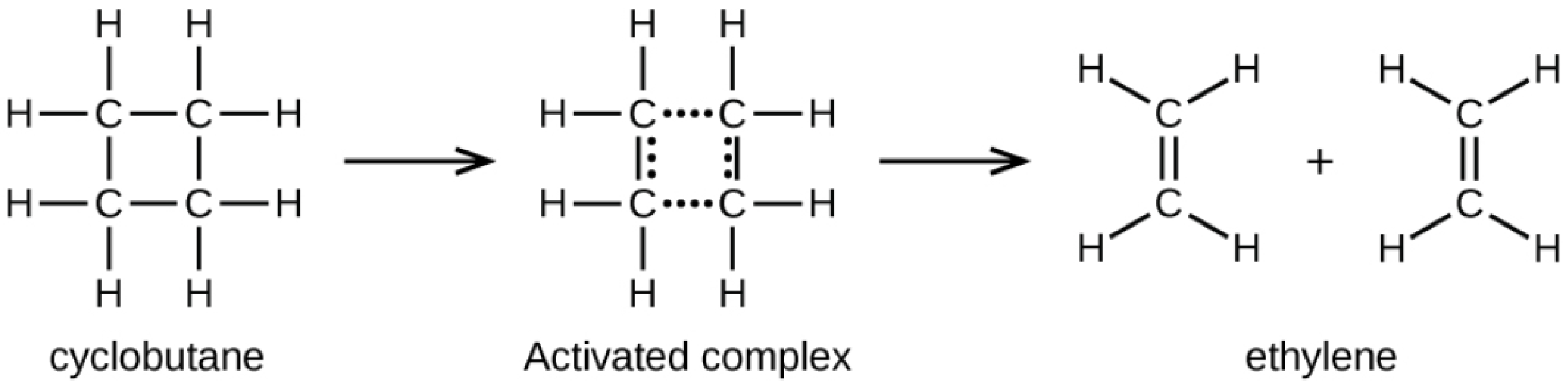
$$A \rightarrow \text{products}$$
$$\text{Rate} = k[A]$$

$$C_4H_8 \rightarrow C_2H_4 + C_2H_4$$

$$\text{Rate} = k[C_4H_8]$$

Unimolecular Elementary Reactions

$$A \rightarrow \text{products}$$
$$\text{Rate} = k[A]$$



Bimolecular Elementary Reactions

$$A + B \rightarrow \text{products}$$
$$\text{Rate} = k[A][B]$$

$$NO_2 + CO \rightarrow NO + CO_2$$

$$\text{Rate} = k[NO_2]\,[CO]$$

Bimolecular Elementary Reactions

$$A + B \rightarrow \text{products}$$
$$\text{Rate} = k[A][B]$$

Bimolecular Elementary Reactions

$$2A \rightarrow \text{products}$$
$$\text{Rate} = k[A]^2$$

$$2HI \rightarrow H_2 + I_2$$

$$\text{Rate} = k[HI]^2$$

Termolecular Elementary Reactions

$$2A + B \rightarrow \text{products}$$
$$\text{Rate} = k[A]^2[B]$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$\text{Rate} = k[NO]^2[O_2]$$

Rate Limiting Step

- A reaction is only as fast as it's slowest step
- Thus, the rate limiting step is the slowest step in a reaction

Rate Limiting Step

Consider the reaction

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

which proceeds by the following series of reactions:

$$2NO_2Cl \leftrightarrow ClO_2 + N_2O + ClO \text{ (fast)}$$

$$N_2O + ClO_2 \leftrightarrow NO_2 + NOCl \text{ (fast)}$$

$$NOCl + ClO \rightarrow NO_2 + Cl_2 \text{ (slow)}$$

Rate Limiting Step

Consider the reaction

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

which proceeds by the following series of reactions:

$$2NO_2Cl \leftrightarrow ClO_2 + N_2O + ClO \text{ (fast)}$$

$$N_2O + ClO_2 \leftrightarrow NO_2 + NOCl \text{ (fast)}$$

$$NOCl + ClO \rightarrow NO_2 + Cl_2 \text{ (slow)}$$

Since this reaction takes the longest, it limits the rate of the reaction and is thus the rate limiting step

Rate Limiting Step and Rate Laws

- Rate laws <u>may not</u> be derived from <u>overall chemical reactions</u>
- However, rate laws for an overall chemical reaction <u>may be</u> derived from the <u>rate limiting step</u>

For a rate limiting step:

$$m[\mathrm{A}] + n[\mathrm{B}] + p[\mathrm{C}] + \cdots \rightarrow \text{products}$$

The rate law of the overall reaction is:

$$\text{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^p \cdots$$

Reaction Mechanisms

The hypochlorite ion undergoes self-oxidation-reduction to give chlorate, ClO_3^-, and chloride ions

$$3\ ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$$

This reaction is thought to occur in two steps:

$$\text{Step 1: } ClO^-(aq) + ClO^-(aq) \rightarrow ClO_2^-(aq) + Cl^-(aq) \quad \text{(Slow)}$$

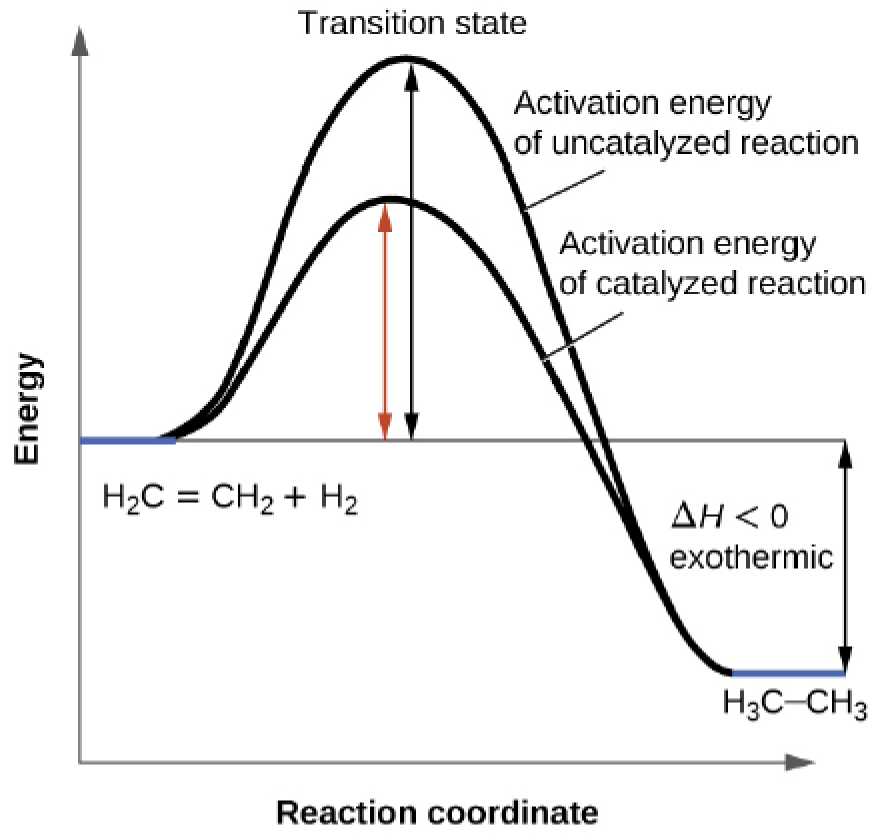
$$\text{Step 2: } ClO_2^-(aq) + ClO^-(aq) \rightarrow ClO_3^-(aq) + Cl^-(aq) \quad \text{(Fast)}$$

What is the molecularity of each step? Identify any intermediates. Write the rate equation for each elementary step. What is the rate equation of the overall reaction?

Catalysis

- Catalysts
  1. Speed up the rate of a reaction by lowering the activation energy
  2. Are regenerated in the process

Lowering activation energy



Lowering the activation energy

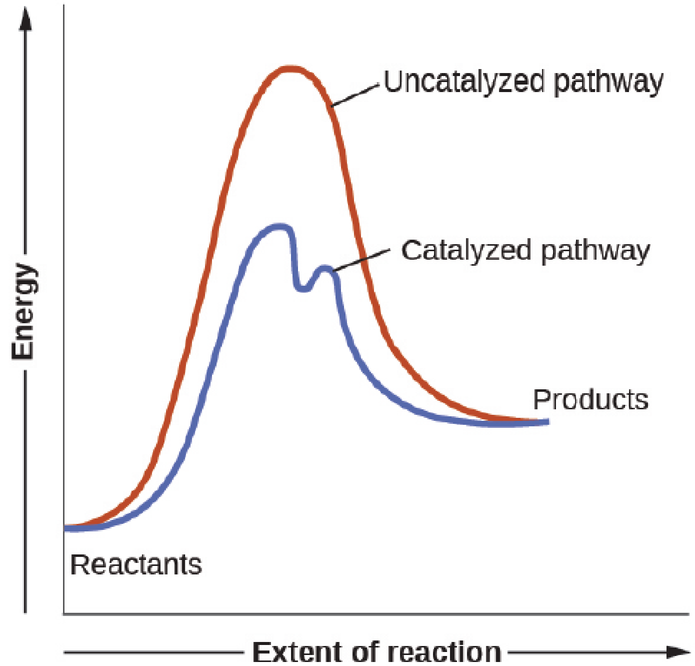


Figure 12.22 This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Catalyst Regeneration

Decomposition of Ozone

$$O_3(g) \rightarrow O_2(g) + O(g) \quad \text{(fast)}$$

$$O(g) + O_3(g) \rightarrow 2O_2(g) \quad \text{(slow)}$$

Catalyst Regeneration

Decomposition of Ozone

$$O_3(g) \rightarrow O_2(g) + O(g) \quad \text{(fast)}$$

$$O(g) + O_3(g) \rightarrow 2O_2(g) \quad \text{(slow)}$$

Nitric Oxide Catalyzed Decomposition

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$O_3(g) \rightarrow O_2(g) + O(g)$$

$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

About 20 million molecules of ozone react with the same number of nitric oxide molecules in every cubic centimeter per second

Homogeneous Catalysts

- Homogeneous catalysts are present in the same phase as the reactants
- They regenerate by:
  - Interacting with a reactant to form an intermediate
  - The intermediate then decomposes or reacts with another reactant to regenerate the original catalyst and form product

Homogeneous Catalysts

Nitric Oxide Catalyzed Decomposition

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$O_3(g) \rightarrow O_2(g) + O(g)$$

$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

Heterogeneous Catalysts

- Heterogeneous catalysts are present in a different phase than the reactants
- They generally provide a surface upon which a reaction can occur

Heterogeneous Catalysis

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

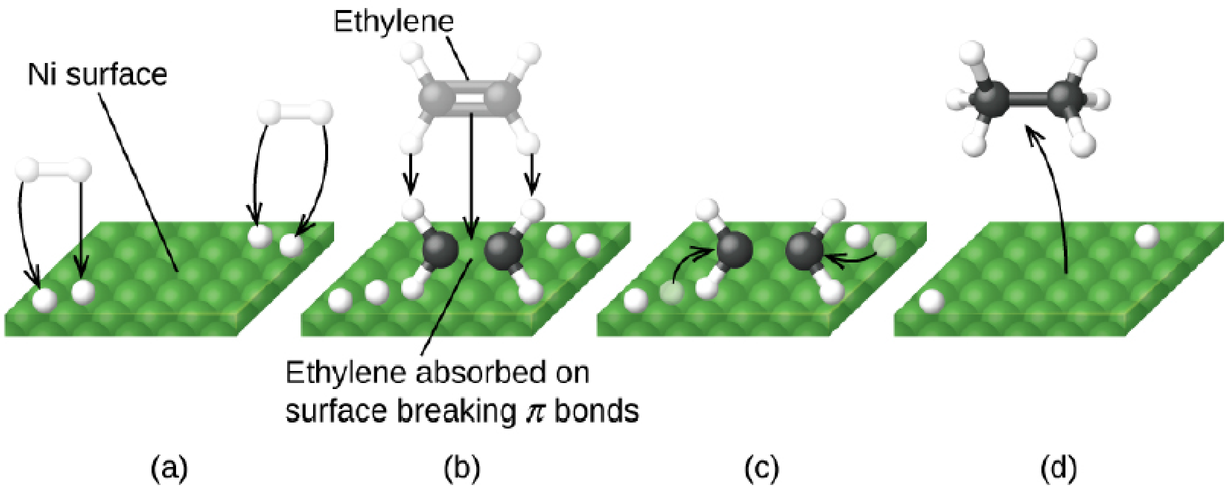


Figure 12.26 There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules escape from the nickel surface, since they are not strongly attracted to nickel.