CHEMISTRY 19.8

MECHANISMS OF CHEMICAL REACTIONS

MDCAT-Focused Notes • Solved Quick Check • Practice

FREE RADICAL Homolysis	POLAR / IONIC Heterolysis	ELECTROPHILE Accepts e^- pair	NUCLEOPHILE Donates e^- pair

1. Reaction Mechanism

Definition

A reaction mechanism is the step-by-step pathway by which a chemical reaction occurs. It shows the breaking and making of bonds and explains how the substrate is converted into products.

2. Main Types of Reaction Mechanisms

Feature	Free-radical	Ionic / polar	MDCAT clue
Bond fission	Homolytic	Heterolytic	How does the bond break?
Main species	Free radicals	Electrophiles / nucleophiles	Look for · or charge
Electron movement	One electron to each atom	Both electrons to one atom	1 e^- vs 2 e^-
Typical example	Chlorination of methane	Nucleophilic substitution	Identify attacker

3. Free-Radical Mechanism

- A free radical contains an unpaired electron, shown by a dot (·).
- Free-radical mechanisms usually involve homolytic fission.
- The three stages are initiation → propagation → termination.

Homolytic fission

A:B → A· + B· | Each atom takes one bonding electron.

4. Chlorination of Methane

Overall reaction

$$CH_4 + Cl_2 \xrightarrow{\text{diffused sunlight}} CH_3Cl + HCl$$

Initiation

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

Propagation

$$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$$

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

Termination

$$Cl\cdot + Cl\cdot \rightarrow Cl_2$$

$$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$$

Memory aid: I → P → T

Initiation = radicals are formed • Propagation = chain continues • Termination = radicals are consumed.

5. Ionic or Polar Mechanism

- Polar mechanisms generally involve heterolytic fission.
- Heterolysis gives ions because both bonding electrons go to one atom.
- The key reactive species are electrophiles and nucleophiles.

Heterolytic fission

$A:B \rightarrow A^+ + :B^-$ | Both bonding electrons go to one atom.

6. Electrophiles

- Electrophile = electron-pair acceptor.
- Usually electron-deficient and often positively or partially positively charged.
- Examples: H^+, NO_2^+, BF_3, $AlCl_3$.
- Electrophiles attack electron-rich regions.

7. Nucleophiles

- Nucleophile = electron-pair donor.
- Usually electron-rich; may be negative or neutral with a lone pair.
- Examples: OH^-, CN^-, Cl^-, NH_3, H_2O.
- Nucleophiles attack electron-deficient/electrophilic centers.

8. Nucleophilic Substitution

Core idea

A nucleophile attacks a saturated electrophilic carbon and replaces a leaving group.

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

- OH^- = nucleophile (attacker)
- Carbon attached to Br = electrophilic carbon
- Br^- = leaving group
- Overall reaction = substitution

9. Recognizing Common Reaction Types

Type	What to look for	Example
Addition	Atoms/groups add across multiple bond	C=C + HBr
Substitution	One atom/group replaces another	$CH_4 + Br_2 \rightarrow CH_3Br + HBr$

Elimination	Groups removed; multiple bond often forms	Haloalkane → alkene + HX
Condensation	Joining with loss of small molecule	Carbonyl + hydrazine → hydrazone + H_2O
Reduction	Gain of H / loss of O	$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$

10. Quick Check 19.6 — Solved

(a) Electrophile, nucleophile or free radical?

Species	Answer / reason
NH_3	Nucleophile — N has a lone pair
$Br\cdot$	Free radical — unpaired electron
H_2O	Nucleophile — O has lone pairs
NO_2^+	Electrophile — electron deficient
$Cl\delta^+$	Electrophilic species — partially positive

(b) Classify the reactions

$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$ — ADDITION

$CH_4 + Br_2 \rightarrow CH_3Br + HBr$ — SUBSTITUTION (free-radical)

$CH_3CH_2CHClCH_3 \rightarrow CH_3CH_2CH{=}CH_2 + HCl$ — ELIMINATION

(c) Classify the reactions

$(CH_3)_2C{=}O + H_2N{-}NH_2 \rightarrow (CH_3)_2C{=}N{-}NH_2 + H_2O$ — CONDENSATION

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$ — REDUCTION

11. MDCAT Practice — 5 MCQs

1. Which species is a nucleophile?

A. NO_2^+
B. H^+
C. NH_3
D. Cl·
Answer: C | NH_3 donates a lone pair.

2. Which process produces free radicals?

A. Heterolysis
B. Homolysis
C. Hydrolysis
D. Condensation
Answer: B | Homolysis gives one electron to each atom.

3. The correct sequence for a free-radical chain reaction is:

A. Propagation → initiation → termination
B. Initiation → termination → propagation
C. Initiation → propagation → termination
D. Termination → propagation → initiation
Answer: C | Radicals are generated, the chain proceeds, then radicals are consumed.

4. In $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$, the attacking species is:

A. CH_3Br
B. Br^-
C. OH^-
D. CH_3OH
Answer: C | OH^- donates an electron pair to carbon.

5. $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$ is best classified as:

A. Oxidation
B. Reduction
C. Addition
D. Elimination
Answer: B | The aldehyde gains hydrogen/reducing equivalents.

12. Short Questions — Practice

1. **Define a reaction mechanism. Name its two major types.**
2. **Differentiate between homolytic and heterolytic fission.**
3. **Define electrophile and nucleophile. Give two examples of each.**
4. **Explain initiation, propagation and termination in chlorination of methane.**
5. **What is nucleophilic substitution? Identify the nucleophile and leaving group in $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$.**

13. MDCAT Rapid Revision

Eight must-remember points

1. Homolysis → free radicals. 2. Heterolysis → ions. 3. Electrophile accepts an electron pair. 4. Nucleophile donates an electron pair. 5. Radical stages = initiation → propagation → termination. 6. Nucleophilic substitution = nucleophile replaces leaving group. 7. Addition occurs across a multiple bond. 8. Elimination often forms a multiple bond.