

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 $\cdot$ 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 ($\cdot$).
- Free-radical mechanisms usually involve homolytic fission.
- The three stages are initiation $\rightarrow$ propagation $\rightarrow$ termination.

Homolytic fission

$A:B \rightarrow A\cdot + B\cdot$ | Each atom takes one bonding electron.

4. Chlorination of Methane

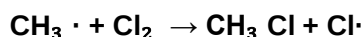
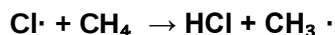
Overall reaction



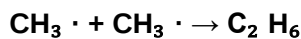
Initiation



Propagation



Termination



Memory aid: I $\rightarrow$ P $\rightarrow$ 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

$\text{A:B} \rightarrow \text{A}^+ + \text{:B}^-$ | 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.

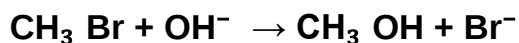
7. Nucleophiles

- 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.



- 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	$\text{C}=\text{C} + \text{HBr}$
Substitution	One atom/group replaces another	$\text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr}$

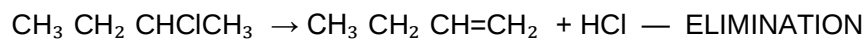
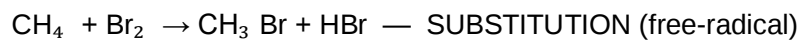
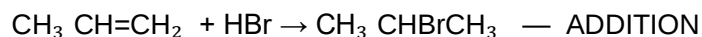
Elimination	Groups removed; multiple bond often forms	Haloalkane $\rightarrow$ alkene + HX
Condensation	Joining with loss of small molecule	Carbonyl + hydrazine $\rightarrow$ hydrazone + H ₂ O
Reduction	Gain of H / loss of O	CH ₃ CHO + 2[H] $\rightarrow$ CH ₃ CH ₂ OH

10. Quick Check 19.6 — Solved

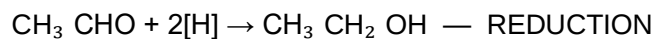
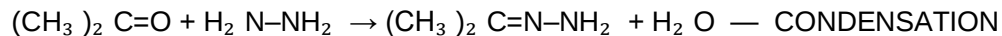
(a) Electrophile, nucleophile or free radical?

Species	Answer / reason
NH ₃	Nucleophile — N has a lone pair
Br·	Free radical — unpaired electron
H ₂ O	Nucleophile — O has lone pairs
NO ₂ ⁺	Electrophile — electron deficient
Cl ^{δ+}	Electrophilic species — partially positive

(b) Classify the reactions



(c) Classify the reactions



11. MDCAT Practice — 5 MCQs

1. Which species is a nucleophile?

- A. NO_2^+
- B. H^+
- C. NH_3
- D. $\text{Cl}\cdot$

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 $\rightarrow$ initiation $\rightarrow$ termination
- B. Initiation $\rightarrow$ termination $\rightarrow$ propagation
- C. Initiation $\rightarrow$ propagation $\rightarrow$ termination
- D. Termination $\rightarrow$ propagation $\rightarrow$ initiation

Answer: C | Radicals are generated, the chain proceeds, then radicals are consumed.

4. In $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$, the attacking species is:

- A. CH_3Br
- B. Br^-
- C. OH^-
- D. CH_3OH

Answer: C | OH^- donates an electron pair to carbon.

5. $\text{CH}_3\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{OH}$ 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 $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$.

13. MDCAT Rapid Revision

Eight must-remember points

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