Haloalkanes NEET Notes – Part 1

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Haloalkanes and Haloarenes – Part 1: Haloalkanes

1. Introduction

- **Haloalkanes (alkyl halides):** Compounds of formula **R–X**, where

  R = alkyl group, X = F, Cl, Br, I.
- **Haloarenes (aryl halides):** Ar–X, where Ar is an aromatic ring (covered later).
- **C–X bond is polar** because X is more electronegative than C.
  - C gets partial + charge (δ^+), X gets partial – charge (δ^-).
  - Therefore carbon attached to halogen is **electrophilic**.

Classification of Alkyl Halides

1. **Number of halogen atoms**
   - **Monohaloalkane**: one halogen
   - **Dihaloalkane**: two halogens
   - **Polyhaloalkane**: ≥ 3 halogens
2. **Nature of carbon attached to X**
   - **Primary (1°):** C attached to one other C
   - **Secondary (2°):** C attached to two C
   - **Tertiary (3°):** C attached to three C

Examples (X = Cl for simplicity):

- 1°: CH_3–CH_2–Cl (1-chloroethane)
- 2°: CH_3–CH(Cl)–CH_3 (2-chloropropane)
- 3°: $(CH_3)_3$C–Cl (tert-butyl chloride)

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2. Structure and Bonding

- Carbon in R–X is **sp^3 hybridised**, roughly tetrahedral (bond angle ~109.5°).
- C–X bond length increases from **C–F < C–Cl < C–Br < C–I**.
- Bond strength: **C–F strongest** (hardest to break), **C–I weakest** (easiest to break).

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3. Methods of Preparation of Alkyl Halides

3.1 From Alcohols

General idea: Replace –OH group by halogen (X).

(A) Using Hydrogen Halides (HX)

Reaction:

ROH + HX → R–X + H_2O

Order of reactivity of alcohols:

3° > 2° > 1° (due to stability of carbocation intermediate).

Conditions:

- For **HI, HBr**: usually presence of **conc. H_2SO_4 / red P** or **H_3PO_4**.
- For **HCl**: less reactive, use **anhydrous $ZnCl_2$** as catalyst

  → **Lucas reagent** = conc. HCl + anhyd. $ZnCl_2$.

Lucas test (visual)

- 3° alcohol → turbidity **immediately**
- 2° alcohol → turbidity in a few **minutes**
- 1° alcohol → **no turbidity at room temp**

(B) Using Phosphorus Halides

1. **PCl_5**:

   $ROH + PCl_5$ → $RCl + POCl_3 + HCl$

2. **PCl_3 / PBr_3 (from red P + Cl_2 / Br_2 in situ):**

   $3ROH + PCl_3$ → $3RCl + H_3PO_3$

3. **PI_3** (from P + I_2):

   $3ROH + PI_3$ → $3RI + H_3PO_3$

These give good yields of alkyl halides.

(C) Using Thionyl Chloride ($SOCl_2$)

$ROH + SOCl_2$ → $RCl + SO_2(g) + HCl(g)$

- Done in presence of **pyridine** (absorbs HCl).
- Very clean because gaseous by-products escape → pure RCl.

3.2 From Hydrocarbons

(A) Free Radical Halogenation of Alkanes

Example:

$CH_4 + Cl_2$ → $CH_3Cl + HCl$ (in presence of hv or 300–400 °C)

Mechanism (chain reaction):

1. **Initiation**

   Cl_2 → $2Cl\bullet$ (homolytic cleavage by light / heat)

2. **Propagation**

   $Cl\bullet + CH_4$ → $CH_3\bullet + HCl$

   $CH_3\bullet + Cl_2$ → $CH_3Cl + Cl\bullet$

3. **Termination**

   Combination of radicals:

   $Cl\bullet + Cl\bullet$ → Cl_2, $CH_3\bullet + CH_3\bullet$ → C_2H_6, etc.

- Gives mixture of mono-, di-, tri-, tetra-halo products.
- Reactivity order of H abstraction: **3° > 2° > 1°**.

(B) Addition of HX to Alkenes

General:

$CH_2=CH-R + HX \rightarrow CH_3-CHX-R$

- Follows **Markovnikov's rule**: "H goes to carbon already having more H".
- For **HBr in presence of peroxides** → **anti-Markovnikov (Kharasch effect)** via free radical mechanism.

(C) Halogenation of Alkenes

$CH_2=CH_2 + X_2 \rightarrow X-CH_2-CH_2-X$ (Vicinal dihalide)

Mechanism: **electrophilic addition**.

(D) From Silver Salts of Carboxylic Acids (Hunsdiecker Reaction)

$RCOOAg + Br_2 \rightarrow R-Br + CO_2 + AgBr$

- Decreases chain length by one carbon (decarboxylation).

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4. Physical Properties of Alkyl Halides

4.1 Boiling Points and Melting Points

- For same alkyl group: **RI > RBr > RCl > RF**

  (because size and mass of halogen ↑ → van der Waals forces ↑).

- For same X: boiling point ↑ as **chain length ↑**,

  but **branching ↓ boiling point** (compact molecule → less surface area).

- **Isomeric dihaloarenes**: para-isomer often has higher m.p. due to better packing.

4.2 Density and Solubility

- Density: increases with **atomic weight of X** and **number of halogens**.

  For given X: **RI most dense, RCl least**.

- Alkyl halides are **practically insoluble in water**

  (because they cannot form hydrogen bonds with water easily)

  but **soluble in organic solvents** like ether, benzene.

- Most are **heavier than water** (except some light chlorides).

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5. Types of Reagents

5.1 Electrophiles

- Electron-deficient species, seek electrons.
- Examples: H^+, Br^+, NO^+, SO_3, PCl_5.

5.2 Nucleophiles

- Species with **lone pair / negative charge** that seek positive centres.
- Examples: OH^-, OR^-, CN^-, NH_3, RNH_2, X^- (Cl^-, Br^-, I^-).

Nucleophilicity trends (very high yield NEET points):

1. **In a given period (same row):**

   Nucleophilicity $\propto$ basicity

   - In gas phase or aprotic solvent: **$F^- > Cl^- > Br^- > I^-$**
   - For neutral bases: **$NH_3 > H_2O$**, etc.

2. **Down a group in protic solvent (H_2O, ROH):**

   - $I^- > Br^- > Cl^- > F^-$

   Because large anions are more polarizable and strongly solvated F^- becomes less available.

3. Bulky groups decrease nucleophilicity

   $(CH_3)_3CO^- < CH_3O^-$

5.3 Solvents

- **Protic solvents**: can donate H^+ / form H-bonds.
  - Examples: H_2O, ROH, NH_3.
- **Aprotic polar solvents**: cannot donate H^+ but have high dielectric constant.
  - Examples: acetone, DMSO, DMF, acetonitrile.

Effect on nucleophilicity:

- In **protic**: large anions best ($I^- > Br^- > Cl^- > F^-$).
- In **aprotic**: reverse order, basicity dominates ($F^- > Cl^- > Br^- > I^-$).

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6. Leaving Group Ability

- Good leaving group = stable after departure.
- **Weaker base = better leaving group.**
- Order: I^- > Br^- > Cl^- >> F^- (F^- is very poor).
- Tosylate, mesylate anions (sulfonate esters) are excellent leaving groups.

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7. Nucleophilic Substitution Reactions

Alkyl halides undergo **substitution** because C–X bond is polar.

Two main mechanisms: **S_n1** and **S_n2**.

7.1 S_n1 Reaction (Unimolecular Nucleophilic Substitution)

Key features (visual picture):

1. **Step 1 (slow, RDS): ionisation → carbocation**

   $R–X \rightarrow R^+ + X^-$

2. **Step 2 (fast): nucleophile attack**

   $R^+ + Nu^- \rightarrow R–Nu$

- Rate law: **Rate = k[alkyl halide]** (depends only on substrate).
- Occurs via **planar carbocation** → nucleophile can attack from both sides → **racemisation** (mixture of enantiomers) with some retention.

Favoured when:

- Substrate forms stable carbocation: **3° > 2° >> 1°**
- Polar protic solvent (water, alcohol).
- Weak or neutral nucleophile (H_2O, ROH).

Energy diagram:

Single big hump (for carbocation formation), then small hump for nucleophile attack.

Example:

$(CH_3)_3C–Br + H_2O \rightarrow (CH_3)_3C–OH + HBr$

7.2 S_n2 Reaction (Bimolecular Nucleophilic Substitution)

Key features (visual picture):

- **Single step, concerted** mechanism.
- Nucleophile attacks carbon **from backside** of C–X bond while X leaves.

Mechanism:

$Nu^- + R–CH_2–X \rightarrow$ [Transition state] $\rightarrow R–CH_2–Nu + X^-$

Transition state: carbon simultaneously bonded partially to Nu and X

(visual: a trigonal bipyramidal arrangement).

Rate law:

Rate = k[alkyl halide][nucleophile]

Stereochemistry – Walden inversion

- For a chiral centre, backside attack gives **inversion of configuration** (like umbrella turning inside out).
- 100% inversion if only S_n2.

Favoured when:

- Substrate: **1° > 2° >> 3°** (steric crowding reduces S_n2).
- Strong nucleophile (OH^-, OR^-, CN^-).
- Polar aprotic solvent (DMSO, DMF, acetone).

Reactivity order (typical example):

Methyl halide > 1° > 2° >> 3° (almost no S_n2 on tertiary).

7.3 Factors Affecting S_n1 vs S_n2 (Very important for NEET)

1. **Structure of alkyl halide**
    - S_n1: 3° > 2° > 1° (carbocation stability).
    - S_n2: methyl > 1° > 2° >> 3° (steric hindrance).
2. **Nature of nucleophile**
    - Strong, negatively charged nucleophile → S_n2.
    - Weak, neutral nucleophile → S_n1.
3. **Solvent**
    - Polar protic → stabilise ions → S_n1 favoured.

  - Polar aprotic → stabilise cations but not anions, nucleophile free → S_n2 favoured.

4. **Leaving group**
    - Better leaving group favours both S_n1 and S_n2, but S_n1 especially because it involves ionisation step.

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8. Important Named Reactions and Applications

8.1 Finkelstein Reaction

- **Halogen exchange**: R–Cl / R–Br + NaI (in dry acetone) → R–I + NaCl / NaBr (ppt).
- Driving force: **NaCl/NaBr precipitate**, shifting equilibrium.
- Used to prepare **alkyl iodides** from cheaper chlorides/bromides.

8.2 Swarts Reaction

- For preparing **alkyl fluorides**:

  R–Cl / R–Br + AgF / Hg_2F_2 / CoF_2 → R–F + AgCl / AgBr etc.

8.3 Hunsdiecker Reaction

Already above: silver salt of carboxylic acid + Br_2 → alkyl bromide (R–Br) with one C less.

8.4 Williamson Ether Synthesis

- From alkyl halide and alkoxide:

  $R–X + R'O^-Na^+ \rightarrow R–O–R' + NaX$ (S_n2 on primary alkyl halide)

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9. Typical NEET-Style Concepts & Tricks

1. **Density order sample**

   For isomeric C_3H_7Br: density increases with mass of halogen same, so depends slightly on packing; often not heavily tested, but remember: **more substituted or multiple halogens → higher density**.

2. **Boiling point vs branching**

   n-C_4H_9Cl > sec-C_4H_9Cl > tert-C_4H_9Cl.

3. **Reactivity of alkyl halides towards S_n1**

   Benzyl > allyl > 3° > 2° > 1° > CH_3X

   (benzyl and allyl have resonance-stabilised carbocations).

4. **Reactivity towards S_n2**

   CH_3X > 1° > 2° (3° almost zero).

5. **Order of leaving group ability**

   OTs^- (tosylate) ≈ OMs^- (mesylate) > I^- > Br^- > Cl^- >> F^-.

6. **Solvolysis**

   When solvent itself acts as nucleophile (e.g., water, alcohol) in S_n1.

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10. Quick Revision Table

Concept	S_n1	S_n2
Steps	2 (carbocation then attack)	1 (concerted)
Rate law	k[substrate]	k[substrate][nucleophile]
Favoured substrate	3° > 2°	CH_3 > 1° > 2°
Nucleophile	weak / neutral	strong, negative
Solvent	polar protic	polar aprotic
Stereochemistry	racemisation (partial inversion)	complete inversion (Walden)

NEET Mock Test – Haloalkanes (Part 1)

Section A: Single Correct MCQs (1–30)

Q1. In haloalkanes, the nature of the C–X bond is best described as:

A. Non-polar due to equal electronegativity of C and X

B. Polar with δ^+ on halogen and δ^- on carbon

C. Polar with δ^+ on carbon and δ^- on halogen

D. Non-polar due to tetrahedral geometry around carbon

Q2. Which of the following correctly represents the general formula for haloalkanes?

A. Ar–X

B. R–X

C. R–OH

D. Ar–OH

Q3. Which of the following statements about bond length and bond strength of C–X bonds is correct?

A. Bond length: C–F > C–Cl > C–Br > C–I

B. Bond length: C–F < C–Cl < C–Br < C–I

C. Bond strength: C–I strongest, C–F weakest

D. Bond strength is independent of halogen size

Q4. Among the following haloalkanes, which represents a tertiary alkyl halide?

A. CH_3CH_2Cl

B. $CH_3CH(Cl)CH_3$

C. $(CH_3)_3CCl$

D. CH_3Cl

Q5. Which of the following reagents is commonly known as Lucas reagent?

A. Conc. HCl

B. Conc. HCl + anhydrous $ZnCl_2$

C. Conc. H_2SO_4 + NaCl

D. HCl gas in dry ether

Q6. In the Lucas test at room temperature, which of the following shows immediate turbidity?

A. Primary alcohol

B. Secondary alcohol

C. Tertiary alcohol

D. All give turbidity at the same rate

Q7. Thionyl chloride ($SOCl_2$) is used to convert alcohols to alkyl chlorides because:

A. The reaction is highly endothermic

B. Only gaseous by-products are formed

C. The reaction does not require a catalyst

D. It produces a mixture of inorganic salts

Q8. Which of the following equations correctly represents the reaction of an alcohol with PCl_5?

A. ROH + PCl_5 → RCl + $POCl_3$ + HCl

B. 3ROH + PCl_5 → 3RCl + H_3PO_4

C. ROH + PCl_5 → RCl + H_3PO_3

D. 3ROH + PCl_5 → 3RCl + $POCl_3$

Q9. The free radical chlorination of methane in the presence of UV light proceeds through:

A. Ionic mechanism

B. Free radical chain mechanism

C. Pericyclic mechanism

D. Concerted nucleophilic substitution

Q10. During free radical halogenation of alkanes, the propagation step involves:

A. Only formation of free radicals from non-radical species

B. Combination of free radicals to form stable molecules

C. Reaction of a free radical with a stable molecule to form a new radical

D. Photochemical cleavage of halogen

Q11. The addition of HBr to an unsymmetrical alkene in the presence of peroxides generally follows:

A. Markovnikov’s rule via ionic mechanism

B. Anti-Markovnikov’s rule via free radical mechanism

C. Markovnikov’s rule via free radical mechanism

D. Anti-Markovnikov’s rule via ionic mechanism

Q12. The addition of Cl_2 to ethene gives:

A. Geminal dichloride

B. Vicinal dichloride

C. Allylic chloride

D. Benzylic chloride

Q13. In the Hunsdiecker reaction, the product obtained from silver salt of a carboxylic acid has:

A. One carbon more than the acid

B. One carbon less than the acid

C. Same number of carbons as the acid

D. Two carbons less than the acid

Q14. Considering boiling points of isomeric C_4H_9Cl, the correct order is:

A. tert-Butyl chloride > sec-Butyl chloride > n-Butyl chloride

B. n-Butyl chloride > sec-Butyl chloride > tert-Butyl chloride

C. sec-Butyl chloride > n-Butyl chloride > tert-Butyl chloride

D. All have the same boiling point

Q15. The low solubility of haloalkanes in water is mainly due to:

A. Strong hydrogen bonding with water

B. Inability to form hydrogen bonds effectively with water

C. Strong covalent interactions with water

D. Their ionic nature in solution

Q16. Which of the following correctly represents the order of leaving group ability among halides?

A. $F^- > Cl^- > Br^- > I^-$

B. $Cl^- > Br^- > I^- > F^-$

C. $I^- > Br^- > Cl^- >> F^-$

D. $Br^- > I^- > Cl^- > F^-$

Q17. Which of the following is a good nucleophile but a poor base in protic solvent?

A. F^-

B. I^-

C. OH^-

D. NH_2^-

Q18. The correct order of nucleophilicity of halide ions in protic solvents is:

A. $F^- > Cl^- > Br^- > I^-$

B. $Cl^- > F^- > Br^- > I^-$

C. $I^- > Br^- > Cl^- > F^-$

D. $Br^- > Cl^- > I^- > F^-$

Q19. The correct order of nucleophilicity of halide ions in aprotic polar solvents is:

A. $F^- > Cl^- > Br^- > I^-$

B. $I^- > Br^- > Cl^- > F^-$

C. $Cl^- > F^- > Br^- > I^-$

D. $Br^- > I^- > Cl^- > F^-$

Q20. Which of the following best describes a polar protic solvent?

A. Solvent capable of donating protons and forming hydrogen bonds

B. Solvent incapable of hydrogen bonding

C. Non-polar solvent with low dielectric constant

D. Solvent with no effect on nucleophilicity

Q21. In an S_n1 reaction, the rate of reaction depends on:

A. Concentration of substrate only

B. Concentration of nucleophile only

C. Product concentration only

D. Concentration of both substrate and nucleophile

Q22. In an S_n2 reaction, the rate of reaction is:

A. Independent of nucleophile concentration

B. Directly proportional to concentration of substrate only

C. Directly proportional to concentration of both substrate and nucleophile

D. Independent of substrate concentration

Q23. Which type of substrate is most reactive towards S_n1 reactions?

A. Primary alkyl halide

B. Secondary alkyl halide

C. Tertiary alkyl halide

D. Methyl halide

Q24. Which type of substrate is most reactive towards S_n2 reactions?

A. Tertiary alkyl halide

B. Secondary alkyl halide

C. Primary alkyl halide

D. Aryl halide

Q25. For an S_n2 reaction at a chiral carbon atom, the stereochemical outcome is:

A. Retention of configuration

B. Inversion of configuration

C. Racemisation

D. No change in configuration

Q26. S_n1 reactions often lead to racemisation because:

A. The transition state is tetrahedral

B. The carbocation intermediate is planar

C. The nucleophile attacks from only one fixed side

D. The leaving group remains attached during nucleophilic attack

Q27. The Finkelstein reaction is used for preparation of:

A. Alkyl fluorides from alkyl bromides

B. Alkyl iodides from alkyl chlorides or bromides

C. Alkyl chlorides from alcohols

D. Aryl iodides from aryl chlorides

Q28. In the Finkelstein reaction, the commonly used solvent is:

A. Water

B. Ethanol

C. Dry acetone

D. Benzene

Q29. The Swarts reaction is specifically used to prepare:

A. Alkyl iodides

B. Alkyl bromides

C. Alkyl fluorides

D. Aryl chlorides

Q30. Williamson ether synthesis between an alkyl halide and an alkoxide ion generally proceeds by:

A. S_n1 mechanism on a tertiary alkyl halide

B. S_n2 mechanism on a primary alkyl halide

C. Radical mechanism

D. Electrophilic addition mechanism

Section B: Assertion–Reason Type (31–35)

For Q31–Q35, choose:

A: Both Assertion and Reason are true, and Reason is the correct explanation of Assertion

B: Both Assertion and Reason are true, but Reason is not the correct explanation of Assertion

C: Assertion is true, but Reason is false

D: Assertion is false, but Reason is true

Q31.

Assertion (A): Tertiary alkyl halides react faster than secondary and primary alkyl halides in S_n1 reactions.

Reason (R): Tertiary carbocations are more stable due to inductive effect and hyperconjugation.

Q32.

Assertion (A): S_n2 reactions are highly sensitive to steric hindrance around the reacting carbon.

Reason (R): In S_n2 reactions, the nucleophile attacks from the side opposite to the leaving group in a single step.

Q33.

Assertion (A): In protic solvents, I^- is a better nucleophile than F^-.

Reason (R): Smaller anions are more strongly solvated in protic solvents, reducing their nucleophilicity.

Q34.

Assertion (A): Free radical halogenation of alkanes proceeds via a chain mechanism.

Reason (R): In the propagation step, radicals react with stable molecules to form new radicals.

Q35.

Assertion (A): Solvolysis of tertiary alkyl halides in water is generally faster than that of primary alkyl halides.

Reason (R): Tertiary carbocations formed in such reactions are more stable than primary carbocations.

Section C: Matching Type (36–40)

Q36. Match the reactions in Column I with their main features in Column II:

Column I

1. S_n1 reaction
2. S_n2 reaction
3. Free radical halogenation

Column II

P. Involves carbocation intermediate

Q. Involves backside attack and inversion

R. Involves chain initiation, propagation, and termination

Options:

A. 1-P, 2-Q, 3-R

B. 1-Q, 2-P, 3-R

C. 1-R, 2-P, 3-Q

D. 1-P, 2-R, 3-Q

Q37. Match the reagents in Column I with their major use in Column II:

Column I

1. NaI in acetone
2. AgF
3. $SOCl_2$ / pyridine

Column II

P. Clean conversion of alcohols to alkyl chlorides

Q. Finkelstein reaction

R. Swarts-type halide exchange to form alkyl fluorides

Options:

A. 1-Q, 2-R, 3-P

B. 1-R, 2-Q, 3-P

C. 1-Q, 2-P, 3-R

D. 1-P, 2-R, 3-Q

Q38. Match the following types of solvents in Column I with examples in Column II:

Column I

1. Protic solvent
2. Aprotic polar solvent

Column II

P. Water

Q. DMSO

Options:

A. 1-P, 2-Q

B. 1-Q, 2-P

C. 1-P, 2-P

D. 1-Q, 2-Q

Q39. Match the following nucleophiles in Column I with their relative steric hindrance in Column II:

Column I

1. CH_3O^-
2. $(CH_3)_3CO^-$

Column II

P. Less sterically hindered

Q. More sterically hindered

Options:

A. 1-P, 2-Q

B. 1-Q, 2-P

C. 1-P, 2-P

D. 1-Q, 2-Q

Q40. Match the following terms in Column I with definitions in Column II:

Column I

1. Electrophile
2. Nucleophile

Column II

P. Electron-deficient species seeking electrons

Q. Electron-rich species seeking positively charged centres

Options:

A. 1-P, 2-Q

B. 1-Q, 2-P

C. 1-P, 2-P

D. 1-Q, 2-Q

Answer Key (for self-checking)

1. C
2. B
3. B
4. C
5. B
6. C
7. B
8. A
9. B
10. C
11. B
12. B
13. B
14. B
15. B
16. C
17. B
18. C
19. A
20. A
21. A
22. C
23. C
24. C
25. B

26. B
27. B
28. C
29. C
30. B
31. A
32. A
33. A
34. A
35. A
36. A
37. A
38. A
39. A
40. A