FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 8
Aliphatic Hydrocarbons

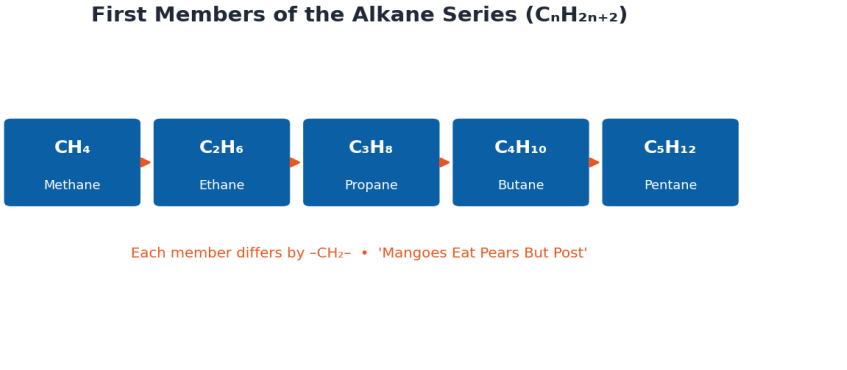

Figure 8.1 — The first members of the alkane homologous series.

1. Chapter Overview

Hydrocarbons are compounds made of only carbon and hydrogen. The aliphatic (open-chain) hydrocarbons are of three kinds: alkanes (saturated, only single bonds), alkenes (one carbon–carbon double bond) and alkynes (one carbon–carbon triple bond). These are the simplest organic compounds and the starting point for making almost every other organic substance — plastics, alcohols, detergents and fuels. This chapter covers how each type is prepared, how they react, and the key ideas of unsaturation, addition reactions and Markownikoff's rule.

2. Learning Objectives

- Distinguish alkanes, alkenes and alkynes and give their general formulas.
- Describe important methods of preparing alkanes, alkenes and alkynes.
- Explain the free-radical substitution (halogenation) of alkanes.
- Describe the addition reactions of alkenes and alkynes.
- State and apply Markownikoff's rule.
- Explain the tests that distinguish saturated from unsaturated hydrocarbons.

3. Key Concepts

3.1 The Three Families

Type	Bonding	General formula	Example
Alkanes	All single bonds (saturated)	C_nH_{2n+2}	CH_4, C_2H_6
Alkenes	One C=C (unsaturated)	C_nH_{2n}	C_2H_4 (ethene)
Alkynes	One C≡C (unsaturated)	C_nH_{2n-2}	C_2H_2 (ethyne)

Memory Trick

Name endings: -ane (single), -ene (double), -yne (triple).

First alkanes: Methane, Ethane, Propane, Butane, Pentane — 'Monkeys Eat Peanut Butter Perfectly'.

3.2 Alkanes — the 'Paraffins'

Alkanes are rather unreactive (the old name 'paraffin' means 'little affinity') because their C–C and C–H single bonds are strong and non-polar. Their most important reactions are combustion (burning in air to give CO_2 and water, releasing large amounts of heat — this is why they are used as fuels) and substitution by halogens in the presence of sunlight.

Free-Radical Halogenation

In sunlight (UV light), methane reacts with chlorine, and a hydrogen atom is replaced step by step by chlorine. The reaction goes by a free-radical chain mechanism with three stages: initiation (Cl_2

splits into chlorine radicals), propagation (radicals react to make products and new radicals), and termination (radicals combine).

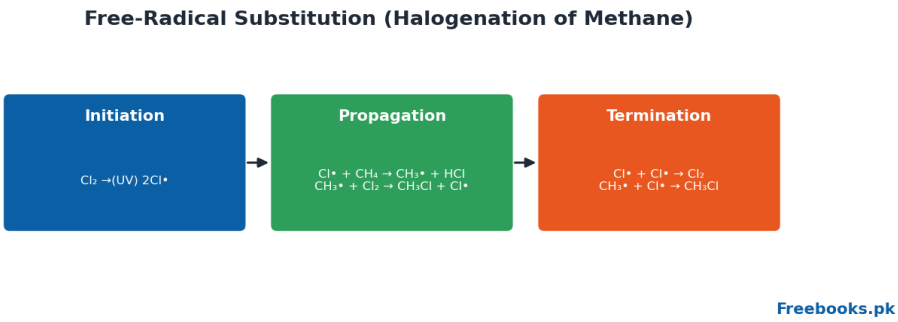

Figure 8.2 — Free-radical substitution of methane by chlorine.

3.3 Alkenes — Reactive Because of the Double Bond

The carbon–carbon double bond is a region of high electron density, so alkenes are much more reactive than alkanes and readily undergo addition reactions, in which the π-bond breaks and atoms add to the two carbons. Common additions include hydrogenation (H_2/Ni → alkane), halogenation (X_2 → dihalide), addition of hydrogen halides (HX → haloalkane), hydration (H_2O/H^+ → alcohol) and polymerisation (many alkene molecules join to form a polymer such as polythene).

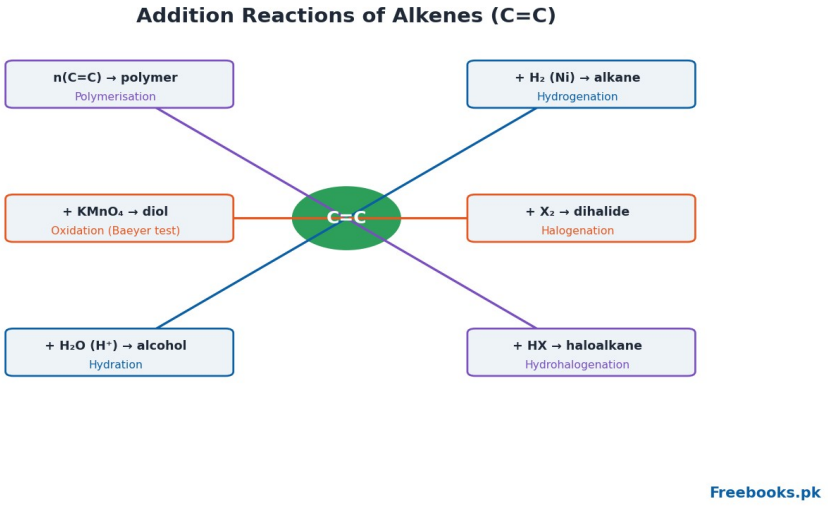

Figure 8.3 — The main addition reactions of alkenes.

Markownikoff's Rule

Markownikoff's Rule

When a hydrogen halide (HX) adds to an unsymmetrical alkene, the hydrogen atom goes to the carbon that already has more hydrogen atoms, and the halogen goes to the carbon with fewer hydrogens.

Example: $CH_3–CH=CH_2$ + HBr → $CH_3–CHBr–CH_3$ (2-bromopropane, the major product).

Teacher's Note

A simple way for students to remember Markownikoff's rule: 'the rich get richer' — the

carbon already rich in hydrogen gets the extra hydrogen.

Tests for Unsaturation

Alkenes (and alkynes) decolourise two reagents that alkanes do not: bromine water (turns from orange to colourless) and dilute alkaline $KMnO_4$ (Baeyer's reagent, turns from purple to colourless). These colour changes are simple laboratory tests for a carbon–carbon multiple bond.

3.4 Alkynes

Alkynes contain a triple bond and, like alkenes, undergo addition reactions. Ethyne (acetylene, C_2H_2) is prepared from calcium carbide and water ($CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$) and is used in oxy-acetylene welding because it burns with a very hot flame. A special feature of terminal alkynes is that the hydrogen on the triple-bonded carbon is weakly acidic, so ethyne reacts with sodium to release hydrogen.

4. Important Definitions

Term	Definition
Hydrocarbon	A compound containing only carbon and hydrogen.
Saturated hydrocarbon	A hydrocarbon with only single C–C bonds (alkane).
Unsaturated hydrocarbon	A hydrocarbon containing a C=C or C≡C bond (alkene/alkyne).
Addition reaction	A reaction in which atoms add across a multiple bond.
Markownikoff's rule	In HX addition to an unsymmetrical alkene, H goes to the carbon with more H atoms.
Free radical	A highly reactive species with an unpaired electron.

5. Formulas / Rules

Must-Know Facts

Formulas: alkane C_nH_{2n+2}, alkene C_nH_{2n}, alkyne C_nH_{2n-2}.
Alkanes: combustion + free-radical substitution (initiation, propagation, termination).
Alkenes: addition (H_2/Ni, X_2, HX, H_2O/H^+, polymerisation).
Markownikoff: H to the C with more H; example $CH_3CH{=}CH_2 + HBr \rightarrow$ 2-bromopropane.
Unsaturation tests: decolourise bromine water and $KMnO_4$.
Ethyne: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$ (used in welding).

6. Diagrams / Illustrations

Key diagrams for revision:

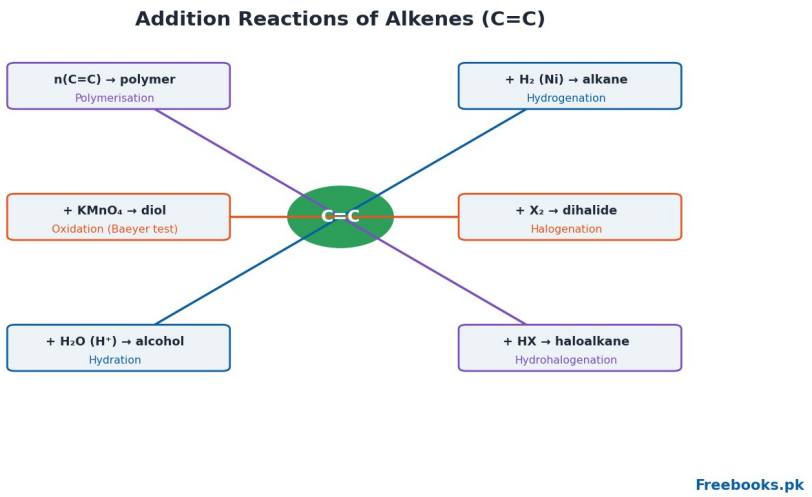

Diagram 1 — Addition reactions of alkenes.

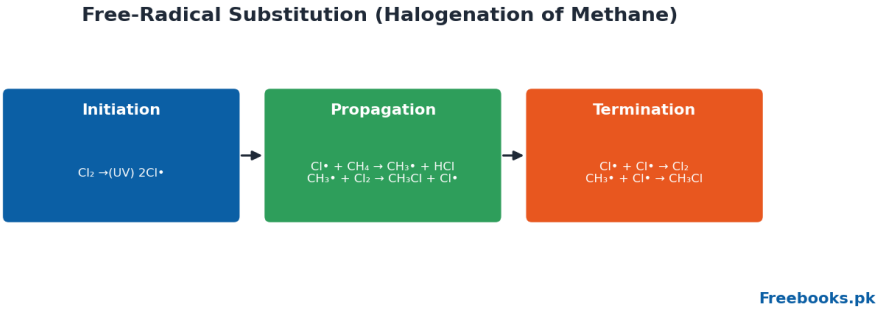

Diagram 2 — Free-radical substitution.

7. Solved Examples

Example 1 — Markownikoff's rule

Q: Predict the major product of $CH_3–CH=CH_2$ + HCl.

Solution: By Markownikoff's rule, H adds to the CH_2 (more hydrogens) and Cl to the middle carbon, giving 2-chloropropane, $CH_3–CHCl–CH_3$, as the major product.

Example 2 — Test for unsaturation

Q: How would you distinguish ethane from ethene in the laboratory?

Solution: Add bromine water. Ethene (unsaturated) decolourises it quickly; ethane (saturated) does not. Alkaline $KMnO_4$ can be used the same way.

Example 3 — Preparation

Q: How is ethyne prepared from calcium carbide?

Solution: Calcium carbide reacts with water: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$, giving ethyne (acetylene) gas.

8. Short Questions

Q1. Why are alkanes called paraffins?
Ans. 'Paraffin' means 'little affinity'; alkanes are fairly unreactive because of their strong, non-polar single bonds.

Q2. What are the three steps of free-radical substitution?
Ans. Initiation, propagation and termination.

Q3. Why are alkenes more reactive than alkanes?
Ans. The C=C double bond is an electron-rich region that readily undergoes addition reactions.

Q4. State Markownikoff's rule.
Ans. When HX adds to an unsymmetrical alkene, hydrogen goes to the carbon with more hydrogen atoms.

Q5. Give two tests for unsaturation.
Ans. Decolourisation of bromine water and of alkaline $KMnO_4$ (Baeyer's reagent).

Q6. How is ethyne prepared?
Ans. From calcium carbide and water: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$.

Q7. Why is ethyne used in welding?
Ans. It burns in oxygen with a very hot flame (oxy-acetylene flame).

Q8. What is produced when ethene is polymerised?
Ans. Polythene (polyethene).

9. Long Questions

Q1. Describe the free-radical halogenation of methane.

When methane and chlorine are mixed in the presence of sunlight (ultraviolet light), the hydrogen atoms of methane are replaced one by one by chlorine atoms in a substitution reaction that proceeds by a free-radical chain mechanism. In the initiation step, ultraviolet light splits a chlorine molecule homolytically into two very reactive chlorine radicals: $Cl_2 \rightarrow 2Cl\bullet$. In the propagation steps a chlorine radical removes a hydrogen atom from methane to give a methyl radical and hydrogen chloride ($Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$), and the methyl radical then reacts with another chlorine molecule to give chloromethane and a new chlorine radical ($CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$); because a radical is regenerated, the chain continues. In the termination steps two radicals combine, ending the chain (for example $Cl\bullet + Cl\bullet \rightarrow Cl_2$, or $CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$). Further substitution can give CH_2Cl_2, $CHCl_3$ and CCl_4.

Q2. Discuss the addition reactions of alkenes.

Because the carbon–carbon double bond is a region of high electron density, alkenes readily undergo addition reactions in which the weaker π-bond breaks and new atoms add to the two carbons, converting the unsaturated compound to a saturated one. With hydrogen and a nickel catalyst an alkene is hydrogenated to the corresponding alkane. With halogens such as bromine it forms a dihalide, and bromine water is decolourised — a test for unsaturation. With hydrogen halides it forms haloalkanes, and for unsymmetrical alkenes the product follows Markownikoff's rule. With water in the presence of an acid catalyst it undergoes hydration to give an alcohol.

Finally, under suitable conditions many alkene molecules add to one another (polymerisation), as when ethene forms polythene. These addition reactions make alkenes valuable building blocks in industry.

Q3. Compare alkanes, alkenes and alkynes in terms of structure and reactivity.

Alkanes, alkenes and alkynes are the three families of aliphatic hydrocarbons and differ in the kind of carbon–carbon bond they contain. Alkanes (C_nH_{2n+2}) are saturated, having only single bonds; their strong, non-polar bonds make them relatively unreactive, so their main reactions are combustion and free-radical substitution. Alkenes (C_nH_{2n}) contain one double bond and alkynes (C_nH_{2n-2}) one triple bond; both are unsaturated and therefore much more reactive, undergoing addition reactions across the multiple bond. Alkenes and alkynes decolourise bromine water and $KMnO_4$, whereas alkanes do not, which provides a simple test to tell them apart. A special feature of terminal alkynes is the weak acidity of the ≡C–H hydrogen, which lets ethyne react with sodium to release hydrogen.

10. Multiple Choice Questions (MCQs)

1. The general formula of alkynes is:
(A) C_nH_{2n+2} (B) C_nH_{2n} (C) C_nH_{2n-2} (D) C_nH_n

2. Halogenation of methane proceeds by a ___ mechanism:
(A) ionic (B) free-radical (C) addition (D) elimination

3. Which decolourises bromine water?
(A) Ethane (B) Ethene (C) Methane (D) Propane

4. Markownikoff's rule applies to addition of ___ to alkenes:
(A) H_2 (B) X_2 (C) HX (D) H_2O only

5. Ethyne is prepared from:
(A) $CaCO_3$ (B) CaC_2 (C) CaO (D) $CaCl_2$

6. Polythene is made by polymerising:
(A) ethyne (B) ethene (C) ethane (D) methane

7. The catalyst for hydrogenation of alkenes is:
(A) Fe (B) Ni (C) V_2O_5 (D) Pt only

8. Baeyer's reagent is:
(A) Br_2 water (B) alkaline $KMnO_4$ (C) conc. H_2SO_4 (D) NaOH

9. Which is a saturated hydrocarbon?
(A) C_2H_4 (B) C_2H_2 (C) C_2H_6 (D) C_3H_6

10. The very hot oxy-acetylene flame uses:
(A) ethene (B) ethyne (C) ethane (D) methane

MCQ Answer Key

1-C 2-B 3-B 4-C 5-B 6-B 7-B 8-B 9-C 10-B

11. Quick Revision / Summary

- Alkanes C_nH_{2n+2} (single), alkenes C_nH_{2n} (double), alkynes C_nH_{2n-2} (triple).

- Alkanes: unreactive; combustion + free-radical substitution (initiation/propagation/termination).
- Alkenes: reactive; addition (H_2/Ni, X_2, HX, H_2O/H^+, polymerisation).
- Markownikoff: H adds to C with more H atoms.
- Unsaturation tests: decolourise bromine water and $KMnO_4$.
- Ethyne from CaC_2 + H_2O; used in welding.

12. Exam Tips

Teacher's Note

Write the free-radical mechanism with all three steps and correct equations — a frequent long question.

Apply Markownikoff's rule carefully to unsymmetrical alkenes; name the major product.

Learn the two unsaturation tests and their colour changes.

Remember the catalyst Ni for hydrogenation and the ethyne preparation from CaC_2.

Do not confuse '-ene' (double) with '-yne' (triple) endings.