KSQUARE CAREER INSTITUTE

HYDROCARBONS

Class 11 Chemistry • Methods of Preparation of Alkanes • NEET / JEE Notes

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Topics Covered

1. Introduction — classification of hydrocarbons
2. Preparation of alkanes: (1) hydrogenation, (2) from alkyl halides (Zn/H^+), (3) Wurtz reaction, (4) Kolbe's electrolysis
3. Mechanisms, important points & reaction cheat-codes
4. Practice questions (class + homework) with solutions
5. Added: decarboxylation, physical properties of alkanes, revision chart

INTRODUCTION

Hydrocarbons are compounds of only carbon and hydrogen. The chapter is studied as: **method of preparation (MOP) → chemical properties → physical properties (last)**.

Class	General formula	Bond type	Example
Alkane	C_nH_{2n+2}	C–C single (sp^3)	CH_4, C_2H_6
Alkene	C_nH_{2n}	C=C double (sp^2)	$CH_2{=}CH_2$
Alkyne	C_nH_{2n-2}	C≡C triple (sp)	HC≡CH
Aromatic (benzene)	C_6H_6	Delocalised π ring	C_6H_6

1. FROM UNSATURATED HYDROCARBONS (HYDROGENATION)

Addition of hydrogen across C=C or C≡C.

Reaction

Reagent: H_2 + catalyst (Ni, Pt or Pd)

$$CH_2{=}CH_2 \xrightarrow{H_2/Ni} CH_3{-}CH_3$$

$$HC{\equiv}CH \xrightarrow{2H_2/Pt} CH_3{-}CH_3$$

- Ni needs high temperature (≈ 523–573 K); **Pt and Pd** work at **room temperature**.
- H_2 alone with an alkene gives a **poor yield** — the metal surface adsorbs both H_2 and the alkene, breaks the H–H bond and adds both H atoms to the **same side** (syn addition).

Important points

Proceeds through a **4-membered cyclic transition state (4MCTS)**.

No intermediate is formed (no C^+, C^- or C•).

Rate of reaction (ROR) ∝ 1 / steric hindrance.

ROR: **alkyne > alkene** (linear alkyne is less hindered than planar alkene).

Heat of hydrogenation (HOH) is **exothermic (ΔH < 0)**; HOH ∝ number of π bonds; if the number of π bonds is the same, **HOH ∝ 1 / stability** of the alkene.

Class questions

Q1. $HC{\equiv}C{-}CH_2{-}CH_2{-}CH{=}CH_2$ + 1 eq H_2/Ni → **$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$** (the triple bond reduces first).

Q2. A diene with one less-substituted and one more-substituted C=C + 1 eq H_2/Pt → the **less hindered (less substituted) double bond** is reduced first.

Q3. Compare ROR and HOH: $CH_2{=}CH_2$ (a) > $CH_3{-}CH{=}CH_2$ (b) > $CH_3{-}CH{=}CH{-}CH_3$ (c) — fewer alkyl groups ⇒ less hindrance & less stable ⇒ higher ROR and higher HOH.

2. FROM ALKYL HALIDES (REDUCTION)

Alkyl halides (**except fluorides**) on reduction with **zinc and dilute HCl** give alkanes.

Reaction

$$R{-}X \xrightarrow{Zn\ /\ dil.\ HCl\ (Zn/H^+)} R{-}H + HX$$

$$Zn + dil.\ HCl \rightarrow ZnCl_2 + H_2\ \ (nascent\ hydrogen)$$

- **R–F** does not react: the C–F bond is very strong (high bond energy).
- Reactivity: **R–Cl < R–Br < R–I** (bond energy decreases ⇒ rate increases).
- Examples: $CH_3CH_2Br \xrightarrow{Zn/H^+} CH_3{-}CH_3$; $(CH_3)_2CHCl \xrightarrow{Zn/H^+} CH_3CH_2CH_3$.

3. WURTZ REACTION

Reaction

$$2\ R{-}X + 2\ Na \xrightarrow{dry\ ether} R{-}R + 2\ NaX$$

$$2\ Na \rightarrow 2\ Na^+ + 2\ e^-\ ;\ R{-}X + e^- \rightarrow R\bullet + X^-\ ;\ R\bullet + R\bullet \rightarrow R{-}R\ (coupling)$$

- **Dry ether** is the solvent (Na reacts with water).
- Examples: 2 CH_3Cl → $CH_3{-}CH_3$; 2 $CH_3CH_2CH_2Br$ → n-hexane; 2 $(CH_3)_2CHBr$ → 2,3-dimethylbutane.

Important points

Useful for preparing alkanes with an **even number of carbon atoms** (**symmetrical** alkanes).

ROR: **R–I > R–Br > R–Cl**.

1° and 2° R–X mainly give the **combination (coupling)** product.

3° R–X mainly gives the **disproportionation** product (alkane + alkene) — bulky radicals prefer not to combine. E.g. t-butyl halide → **isobutane + isobutene**.

Methane cannot be prepared by Wurtz reaction.

Vinyl, aryl and alkynyl halides do not give the normal Wurtz reaction.

Mixed (Cross) Wurtz Reaction

- Two different halides (R–X + R′–X) give **three alkanes**: R–R, R′–R′ and R–R′ — difficult to separate.
- E.g. $CH_3Cl + CH_3CH_2Cl$ → **ethane + butane + propane** (total 3).
- So **odd-carbon alkanes** are not prepared well by Wurtz.

Types of Wurtz Reaction

Type	Description	Example
Intermolecular	Between two molecules: 2 R–X → R–R	2 $CH_3Br \rightarrow C_2H_6$
Intramolecular	Within the same molecule (dihalide) → ring or alkene	1,3-dihalide → cyclopropane; Cl–CH_2–CH_2–Cl → CH_2=CH_2

NEET Point / PYQ Alert

Intramolecular reactions are **faster** than intermolecular, but the **product must be stable** — **aromatic** products form; **anti-aromatic** (e.g. cyclobutadiene) do not (unstable at room temperature) — then the intermolecular product forms instead.

PRACTICE — PART 1

Q1. Write the product: an alkene/alkyne chain + H_2 (cat. Pd/C).

Answer: The corresponding alkane — all C=C/C≡C become single bonds; the carbon skeleton is unchanged.

Q2. Write the major products with Na/dry ether: (i) bromo-cyclopentylmethane type halide (ii) 1,4- / 1,5-dibromoalkane

Answer: (i) coupling dimer R–R; (ii) intramolecular cyclisation to the cycloalkane — Homework.

Q3. Which among the following compounds will give the Wurtz reaction?

(a) CH_2=CHBr
(b) C_6H_5–Br
(c) CH_2=CH–CH_2–Br
(d) HC≡C–Br

Answer: (c) — Allyl bromide (sp^3 C–Br); vinyl, aryl and alkynyl halides do not.

Q4. An optically active hydrocarbon C_6H_{12} gives an optically inactive C_6H_{14} on catalytic hydrogenation. The compound is

(a) $CH_3–CH_2–C(CH_3)=CH–CH_3$
(b) $CH_3–C(CH_3)_2–CH=CH_2$ type
(c) $CH_3–CH_2–CH(CH_3)–CH=CH_2$
(d) All

Answer: (c) — 3-Methylpent-1-ene (chiral C3) → 3-methylpentane (two identical ethyl groups ⇒ achiral).

Q5. On catalytic reduction (H_2/Pt), how many alkenes give 2-methylbutane?

(a) 1
(b) 2
(c) 3
(d) 4

Answer: (c) — 2-methylbut-1-ene, 2-methylbut-2-ene, 3-methylbut-1-ene.

Q6. Which compound can be best prepared by the Wurtz reaction?

(a) Isobutane
(b) n-Butane
(c) n-Pentane
(d) Isopentane

Answer: (b) — Symmetrical, even-carbon: 2 CH_3CH_2Br → n-butane.

Q7. On catalytic reduction with H_2/Pt, how many alkenes give n-butane?

(a) 1
(b) 2
(c) 3
(d) 4

Answer: (c) — But-1-ene, cis-but-2-ene, trans-but-2-ene.

4. KOLBE'S ELECTROLYTIC METHOD

An **aqueous solution of sodium or potassium salt of a carboxylic acid** on **electrolysis** gives an alkane with an **even number of carbon atoms** at the **anode**.

Reaction

$$2\ R–COO^-K^+ + 2\ H_2O \xrightarrow{\text{electrolysis}} R–R + 2\ CO_2 + H_2 + 2\ KOH$$

e.g. $2\ CH_3COONa + 2\ H_2O \rightarrow CH_3–CH_3 + 2\ CO_2 + H_2 + 2\ NaOH$

Mechanism

Electrode	Process
Ionisation	$2\ R–COO^-K^+ \rightarrow 2\ R–COO^- + 2\ K^+$; $2\ H_2O \rightarrow 2\ OH^- + 2\ H^+$
At anode (oxidation)	$2\ R–COO^- \rightarrow 2\ R–COO\bullet + 2\ e^- \rightarrow 2\ R\bullet + 2\ CO_2\uparrow$; $R\bullet + R\bullet \rightarrow$ **R–R**
At cathode (reduction)	$2\ H^+ + 2\ e^- \rightarrow$ **$H_2\uparrow$**

Important points

Alkane & CO_2 are evolved at the **anode** (the PDF slide says "alkene" — it should be **alkane**).

H_2 is evolved at the **cathode**.

Solution after electrolysis is **basic (pH ↑)** due to KOH/NaOH formation.

Methane cannot be prepared by Kolbe's method.

NEET Point / PYQ Alert

Reaction cheat code (RCC): Kolbe and Wurtz both make **radicals R• and join them (R–R)** — "Kolbe, Wurtz ke chakkar mein radical lelo."

Any product question: remove –COOK (Kolbe) or –X (Wurtz), then **join the two R groups**.

Kolbe — class examples

Salt	Product
Potassium 2-methylbutanoate type (R–COOK, ×2)	Dimer R–R (join at the carbon that carried –COOK)
Potassium succinate (KOOC–CH_2–CH_2–COOK)	**Ethene** (CH_2=CH_2)
Potassium maleate/fumarate (KOOC–CH=CH–COOK)	**Ethyne** (HC≡CH)
Cyclic 1,2-dicarboxylate (on a ring)	Cycloalkene (new C=C in the ring)

DECARBOXYLATION (ADDITIONAL TOPIC)

Soda-lime decarboxylation

$$R\text{–}COONa + NaOH \xrightarrow{CaO,\ \Delta} R\text{–}H + Na_2CO_3$$

$$\text{e.g. } CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$$

- Product has **one carbon less** than the acid — the best way to prepare **methane**.
- Soda-lime = NaOH + CaO (CaO keeps NaOH dry and non-corrosive).

PHYSICAL PROPERTIES OF ALKANES (ADDITIONAL TOPIC)

- Non-polar; C_1–C_4 gases, C_5–C_{17} liquids, C_{18}+ solids at 298 K.
- **Boiling point increases** with molecular mass (stronger van der Waals forces).
- Among isomers, **branching decreases boiling point** (less surface area): n-pentane (309 K) > isopentane (301 K) > neopentane (282.5 K).
- Insoluble in water, soluble in non-polar solvents ("like dissolves like").

REVISION CHART

#	Method	Reagent	Function / note
1	Hydrogenation	H_2 + Ni / Pt / Pd	>C=C< or –C≡C– → alkane (H, H added; π bond broken)
2	Reduction of R–X	Zn / H^+ (dil. HCl)	R–X → R–H (X replaced by H); R–F does not react
3	Wurtz reaction	Na / dry ether	2 R–X → R–R (even C, symmetrical)
4	Kolbe's electrolysis	Electrolysis of aq. RCOONa/K	2 $R–COO^-$ → R–R + 2 CO_2 (even C)
5	Decarboxylation	NaOH + CaO, Δ	R–COONa → R–H (one C less)

QUICK REVISION

- Hydrogenation: 4MCTS, no intermediate, syn addition; ROR alkyne > alkene; ROR ∝ 1/steric hindrance; HOH ∝ 1/stability.
- R–X + Zn/HCl → R–H; reactivity R–I > R–Br > R–Cl; R–F inert.
- Wurtz: Na/dry ether; even-carbon symmetrical alkanes; 3° R–X → disproportionation; CH_4 not possible; cross-Wurtz gives 3 alkanes.
- Kolbe: anode — alkane + CO_2; cathode — H_2; solution becomes basic; CH_4 not possible.
- Decarboxylation: one carbon less; prepares CH_4.

Notes revise 2 times, homework done — practice is the key!