Unit 14 · Hydrocarbons

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Organic Chemistry (Units 12–15 together): 18 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: B + HBr → C, then C + Na in dry ether (Wurtz) → D, C_6H_{14}; long: ozonolysis of an alkene in two steps, its H_2/Ni product, a test for unsaturation, the use of ozonolysis
- **MCQ (1 mark)**: sp^3, sp^2, sp; C_nH_{2n+2}; masses 16, 30, 44; CH_3COONa + soda lime → CH_4; Wurtz equation; alc. KOH → ethene; match Markovnikov, Wurtz, ozonolysis, Baeyer; reagent tables; paraffins
- **Short (5 marks, in parts)**
  - isomers of C_4H_{10}; why the peroxide effect only with HBr; why Wurtz is poor for odd alkanes
  - an example each: Wurtz, Kolbe, decarboxylation, Markovnikov, dehydrohalogenation
  - identify P–T in a reaction table; methane → ethyne; but-2-ene vs octane by a test
  - Wurtz vs decarboxylation; Markovnikov vs anti-Markovnikov; olefins vs paraffins
  - ozonolysis products of five alkenes; addition vs substitution; most acidic of C_2H_6, C_2H_4, C_2H_2; orbital pictures of CH_4, C_2H_4, C_2H_2
- **Long (8 marks)**: alkanes saturated, alkynes more acidic, nitration and sulphonation; three physical and five chemical properties compared; P–W reaction table; methane → ethene; what happens when (eight reactions)

Key terms

Alkanes (paraffins, "little affinity"): C_nH_{2n+2}, single bonds, **sp^3**, 109.5°; **substitution**.

Alkenes (olefins): C_nH_{2n}, one C=C, **sp^2**, 120°, planar; **addition**.

Alkynes: C_nH_{2n-2}, one C≡C, **sp**, 180°, linear; addition (twice); terminal ones acidic.

Primary, secondary, tertiary, quaternary carbon (1°, 2°, 3°, 4°): joined to 1, 2, 3, 4 other carbons.

Wurtz reaction: 2R–X + 2Na (dry ether) → R–R + 2NaX.

Decarboxylation: RCOONa + NaOH (CaO, heat) → R–H + Na_2CO_3; one carbon fewer.

Dehydrohalogenation: removing HX with **alcoholic** KOH → alkene (β-elimination).

Markovnikov's rule: in HX + an unsymmetrical alkene, H goes to the C=C carbon with **more H**, X to the one with fewer.

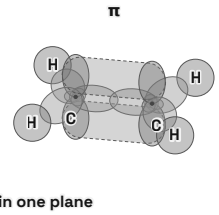
Peroxide (Kharasch) effect: with peroxide, **HBr only** adds against Markovnikov (Br to the carbon with more H).

Saytzeff's rule: elimination gives mainly the **more substituted** alkene.

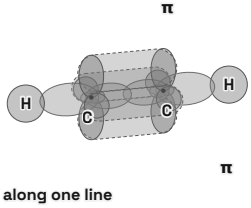
Ozonolysis: O_3 then Zn/H_2O cuts the C=C into two C=O compounds.

Structure

	C–C	C=C	C≡C
hybrid	sp^3	sp^2	sp
bonds	1σ	$1\sigma + 1\pi$	$1\sigma + 2\pi$
shape	tetrahedral 109.5°	planar 120°	linear 180°
length (pm)	154	134	120
energy (kJ/mol)	348	614	839



Ethene: sp^2 σ framework; the π bond's cloud above and below the plane.



Ethyne: sp σ framework, two π bonds at right angles.

- π weaker than σ, its electrons exposed → alkenes, alkynes **add**; alkanes, all σ and hardly polar, only **substitute**

- isomers: C_4H_{10} butane, 2-methylpropane; C_5H_{12} pentane (b.p. 36 °C), 2-methylbutane (28), 2,2-dimethylpropane (9.5): more branched, lower b.p.; C_6 5, C_7 9, C_8 18

Alkanes

Preparation

- reduction: $R{-}X + 2\,[H] \xrightarrow{Zn+HCl} R{-}H + HX$; $C_2H_5Cl + 2\,[H] \longrightarrow C_2H_6 + HCl$
- **Wurtz**: $2\,C_2H_5Cl + 2\,Na \xrightarrow{\text{dry ether}} C_4H_{10} + 2\,NaCl$ (butane); gives even, symmetrical alkanes; for propane $CH_3Cl + C_2H_5Cl$ give a mixture of ethane, propane, butane (hard to separate)
- **decarboxylation**: $CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$ (soda lime)
- hydrogenation: $CH_3CH{=}CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3CH_2CH_3$ (Ni about 200–300 °C; Pt, Pd cold)
- **Kolbe** (below)

Reactions

- **halogenation** (UV light or 400 °C, free radicals): $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl \rightarrow CH_2Cl_2 \rightarrow CHCl_3 \rightarrow CCl_4$; propane gives 1- and 2-chloropropane; Br_2 slower; I_2 hardly (reversible: HI reduces it back)
  - initiation $Cl_2 \longrightarrow 2\,Cl^{\bullet}$; propagation $Cl^{\bullet} + CH_4 \longrightarrow HCl + CH_3{}^{\bullet}$, $CH_3{}^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$; termination two radicals join
- **nitration**: HNO_3 vapor, 400–500 °C: $C_2H_6 + HNO_3 \longrightarrow C_2H_5NO_2 + H_2O$ (some CH_3NO_2 too)
- **sulphonation**: fuming H_2SO_4, hexane and up: $R{-}H + H_2SO_4 \longrightarrow R{-}SO_3H + H_2O$
- **combustion**: $2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$; little air → CO, soot
- **catalytic oxidation**: $2\,CH_4 + O_2 \xrightarrow[200\,^\circ C]{Cu,\ 100\ atm} 2\,CH_3OH$; $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

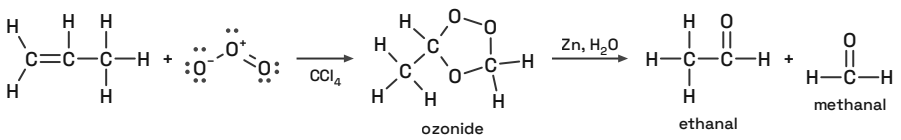
Alkenes

Preparation

- dehydration: $C_2H_5OH \xrightarrow[170\,^\circ C]{\text{conc. } H_2SO_4} CH_2{=}CH_2 + H_2O$ (or Al_2O_3, 350 °C); butan-2-ol → mainly but-2-ene (Saytzeff)
- **dehydrohalogenation**: $CH_3CH_2Br + KOH(alc) \longrightarrow CH_2{=}CH_2 + KBr + H_2O$; 3° > 2° > 1°; aqueous KOH gives the alcohol instead
- Lindlar's catalyst ($Pd/CaCO_3$ poisoned with lead acetate, quinoline): $HC{\equiv}CH + H_2 \longrightarrow CH_2{=}CH_2$
- vicinal dihalide + Zn dust: $CH_2Br{-}CH_2Br + Zn \longrightarrow CH_2{=}CH_2 + ZnBr_2$

Reactions (electrophilic **addition**)

- H_2 (Ni) → alkane; $CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br{-}CH_2Br$
- HX, Markovnikov: $CH_3CH{=}CH_2 + HBr \longrightarrow CH_3CHBrCH_3$ (via the more stable 2° carbocation; 3° > 2° > 1°)
- with peroxide: $CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$ (Br• adds first; HCl's bond too strong, I• too weak)
- water (H^+): $CH_3CH{=}CH_2 + H_2O \longrightarrow CH_3CH(OH)CH_3$; cold conc. H_2SO_4 → alkyl hydrogen sulphate (boil with water → alcohol)
- **ozonolysis**: alkene + O_3 (CCl_4, cold) → ozonide; + Zn/H_2O → carbonyls (Zn removes H_2O_2)



Ozonolysis: O_3 adds across the C=C as an ozonide; zinc and water split it into two carbonyl compounds.

Alkene	Products
ethene	2 HCHO
propene	CH_3CHO + HCHO
but-1-ene	CH_3CH_2CHO + HCHO
but-2-ene	2 CH_3CHO
2-methylbut-2-ene	CH_3COCH_3 + CH_3CHO
2,3-dimethylbut-2-ene	2 CH_3COCH_3

- use: finds **where the C=C is**: join the two C=O carbons with a double bond
- polymerization: n $CH_2{=}CH_2$ → $(-CH_2{-}CH_2{-})_n$, polythene

Model paper chain: propene (B) + HBr → **2-bromopropane** (C); 2C + 2Na (dry ether) → **2,3-dimethylbutane** (D), $(CH_3)_2CH{-}CH(CH_3)_2$, C_6H_{14}

Alkynes

Preparation

- Berthelot: $2\,C + H_2 \xrightarrow{\text{electric arc}} HC{\equiv}CH$
- vicinal dihalide: $CH_2Br{-}CH_2Br + KOH(alc) \longrightarrow CH_2{=}CHBr$, then $CH_2{=}CHBr + NaNH_2 \longrightarrow HC{\equiv}CH + NaBr + NH_3$
- $2\,CHCl_3 + 6\,Ag \xrightarrow{\Delta} HC{\equiv}CH + 6\,AgCl$ (or CHI_3)

Reactions

- H_2/Ni → alkene → alkane (Lindlar: stops at the cis-alkene)
- HX twice, Markovnikov: $HC{\equiv}CH + HCl \longrightarrow CH_2{=}CHCl$ (vinyl chloride) → CH_3CHCl_2; Br_2: → $CHBr{=}CHBr \rightarrow CHBr_2CHBr_2$
- hydration (1% $HgSO_4$, dil. H_2SO_4, 333 K): enol → $HC{\equiv}CH + H_2O \longrightarrow CH_3CHO$ (only ethyne gives an aldehyde); propyne → **propanone**
- red-hot iron tube (873 K): $3\,HC{\equiv}CH \longrightarrow C_6H_6$
- **acidic** (terminal ≡C–H): sp carbon, 50% s character, holds electrons closest: pKa ethyne 25, ethene 44, ethane 50
  - $2\,HC{\equiv}CH + 2\,Na \xrightarrow{\text{liq. } NH_3} 2\,HC{\equiv}CNa + H_2$
  - Tollens' $[Ag(NH_3)_2]OH$ → **white** $AgC{\equiv}CAg$; ammoniacal Cu_2Cl_2 → **red** $CuC{\equiv}CCu$ (alkenes, but-2-yne: none); dry acetylides explode

Tests for unsaturation

- **bromine water** (reddish brown) → **colorless**: $CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$; ethyne takes twice as much
- **Baeyer's reagent** (cold, dilute, alkaline $KMnO_4$, purple) → colorless + brown MnO_2: $3\,C_2H_4 + 2\,KMnO_4 + 4\,H_2O \longrightarrow 3\,C_2H_4(OH)_2 + 2\,MnO_2 + 2\,KOH$ (ethane-1,2-diol)
- an alkane (octane) leaves both unchanged; but-2-ene decolorizes them

Kolbe's electrolysis

- conc. sodium salt solution; **anode**: $2\,RCOO^- \longrightarrow R{-}R + 2\,CO_2 + 2\,e^-$; **cathode**: $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$ (not Na)
- $2\,CH_3COONa + 2\,H_2O \longrightarrow C_2H_6 + 2\,CO_2 + H_2 + 2\,NaOH$; sodium propanoate → butane
- potassium succinate → **ethene**; sodium maleate → **ethyne** (+ $2CO_2$ at the anode, H_2 + KOH/NaOH at the cathode)

Conversions

- **methane → ethane**: $CH_4 \xrightarrow{Cl_2,\ UV} CH_3Cl \xrightarrow{Na,\ \text{dry ether}} C_2H_6$
- **ethane to ethene**: $C_2H_6 \xrightarrow{Cl_2,\ UV} C_2H_5Cl \xrightarrow{\text{alc. KOH}} CH_2{=}CH_2$
- **ethene to ethyne**: $C_2H_4 \xrightarrow{Br_2} C_2H_4Br_2$, then alc. KOH, then $NaNH_2$ → $HC{\equiv}CH$

	Alkanes	Alkenes	Alkynes
state	C_1–C_4 gas, C_5–C_{17} liquid	C_2–C_4 gas	C_2–C_4 gas (but-2-yne liquid)
water	insoluble, float (less dense)	insoluble	insoluble (ethyne slightly)
acidic	no	no	terminal ones, weakly
typical reaction	substitution	addition	addition, ×2
Br_2 water, Baeyer	no change	decolorized	decolorized
Tollens', Cu_2Cl_2	no	no	ppt (terminal)
burn	clean flame	smoky	very sooty

COMMON MISTAKES

✗ chlorination products 1,1-dichloromethane…
✓ **dichloromethane, trichloromethane, tetrachloromethane** (no locants on one carbon).

✗ propane chlorinated over Ni, Pt
✓ **UV light** or heat; gives both 1- and 2-chloropropane.

✗ Baeyer's reagent is bromine in CCl_4
✓ **cold dilute alkaline $KMnO_4$**.

✗ Lindlar's catalyst $Pd/BaSO_4$
✓ **$Pd/CaCO_3$** with lead acetate and quinoline ($Pd/BaSO_4$ + quinoline works similarly).

✗ Kolbe: Na^+ discharged at the cathode
✓ **water** is reduced: $H_2 + OH^-$.

✗ peroxide effect with HCl
✓ **HBr only**.

✗ propyne $CH_3{-}C{\equiv}CH_2$
✓ **$CH_3{-}C{\equiv}CH$**.

✗ R–X + 2[H] → R–X + HX
✓ **R–H** + HX.

✗ alkynes are acidic
✓ only **terminal** alkynes.

✗ Kharash effect
✓ **Kharasch**.