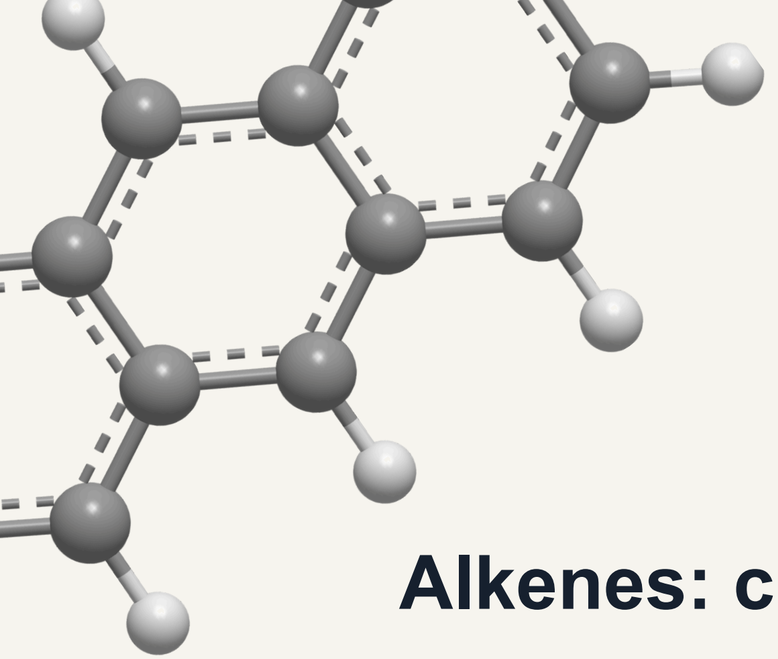
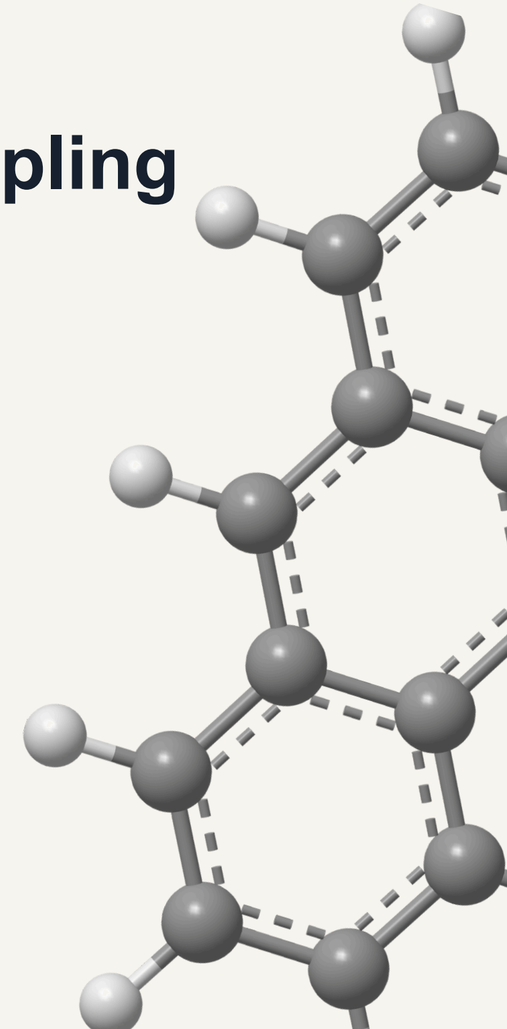


Lecture 8

Alkenes: chemical properties. Electrophile coupling reaction mechanism and Harash effect.



Lecture: PhD, acc. professor: Kudaibergenova B.M

Aim and Objectives

Aim: to investigate the chemical properties of alkenes, explain electrophilic addition, and study the Kharasch effect as anti-Markovnikov addition.

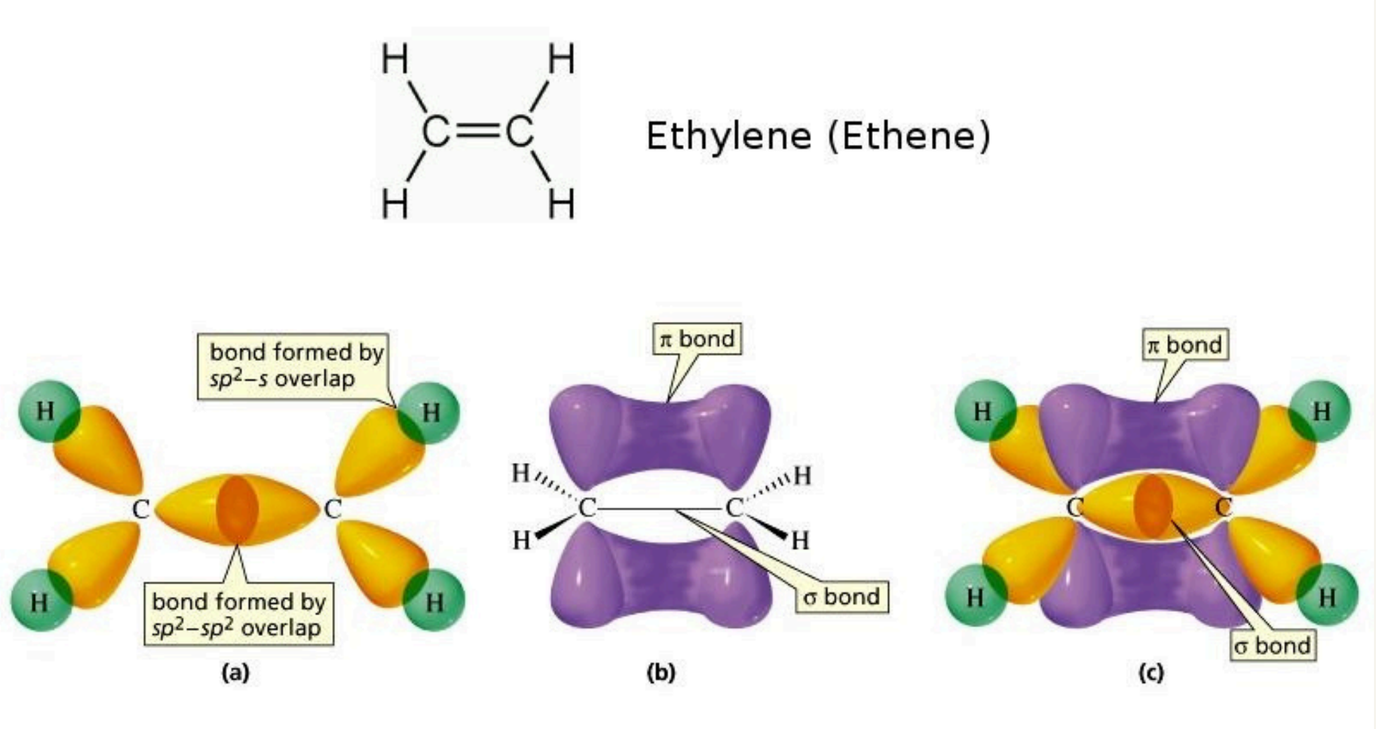
- 1. Describe structure and properties of alkenes
- 2. Investigate reactions of the C=C bond
- 3. Explain hydrogenation, halogenation, hydration, hydrohalogenation
- 4. Examine the electrophilic addition mechanism
- 5. Understand carbocation formation and stability
- 6. Explain Markovnikov’s rule with examples
- 7. Study the free-radical mechanism of the Kharasch effect
- 8. Compare Markovnikov and anti-Markovnikov addition
- 9. Identify industrial applications of alkenes

Introduction to Alkenes

General formula (acyclic, one C=C):

C_nH_{2n}

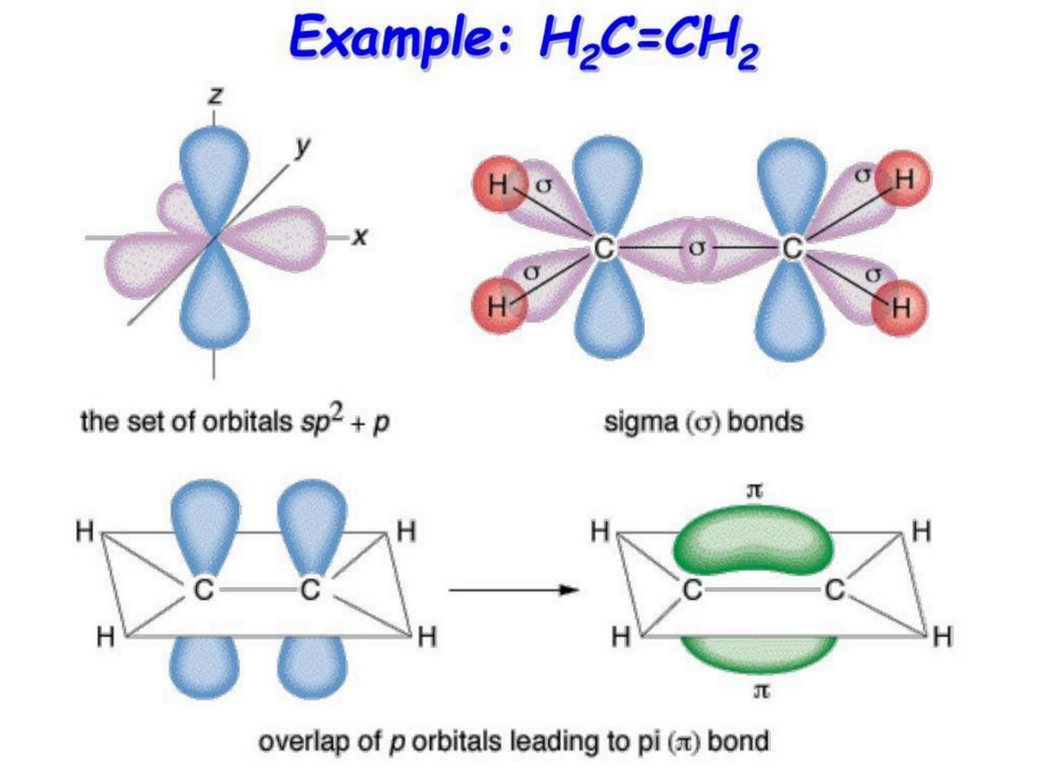
- Unsaturated hydrocarbons with at least one C=C bond
- Contain both sigma (σ) and pi (π) bonds
- Double-bond carbons are sp² hybridized; angles ≈ 120°
- The π bond is weak and highly reactive
- Widely used in the chemical industry



Structure and Reactivity

$CH_2=CH_2 + H_2 \rightarrow CH_3–CH_3$

Ethene → ethane



- The C=C bond: one strong σ bond and one weaker π bond
- σ bond: overlap of sp² hybrid orbitals
- π bond: sideways overlap of unhybridized p orbitals
- π electrons lie above and below the molecular plane, accessible to electrophiles
- In addition, the π bond breaks and new σ bonds form

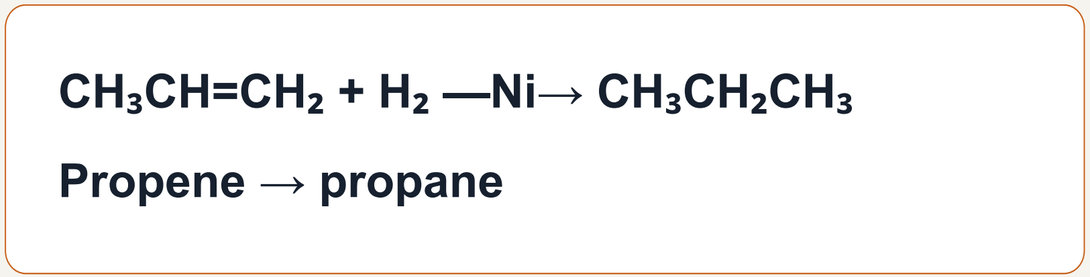
Main Chemical Properties

Reaction	Reagent	Main product
Hydrogenation	H_2 / Ni	Alkane
Halogenation	Br_2 or Cl_2	Dihaloalkane
Hydrohalogenation	HCl, HBr, HI	Haloalkane
Hydration	H_2O / H^+	Alcohol
Oxidation	$KMnO_4$	Diol or cleavage products
Polymerization	Catalyst or initiator	Polymer

Key for the synthesis of organic compounds.

Hydrogenation of Alkenes

- Addition of H_2 gives a saturated hydrocarbon
- 1. Alkene and H_2 adsorb on the catalyst surface
- 2. H_2 dissociates into adsorbed H atoms
- 3. H atoms transfer to the double-bond carbons
- 4. The saturated product is released

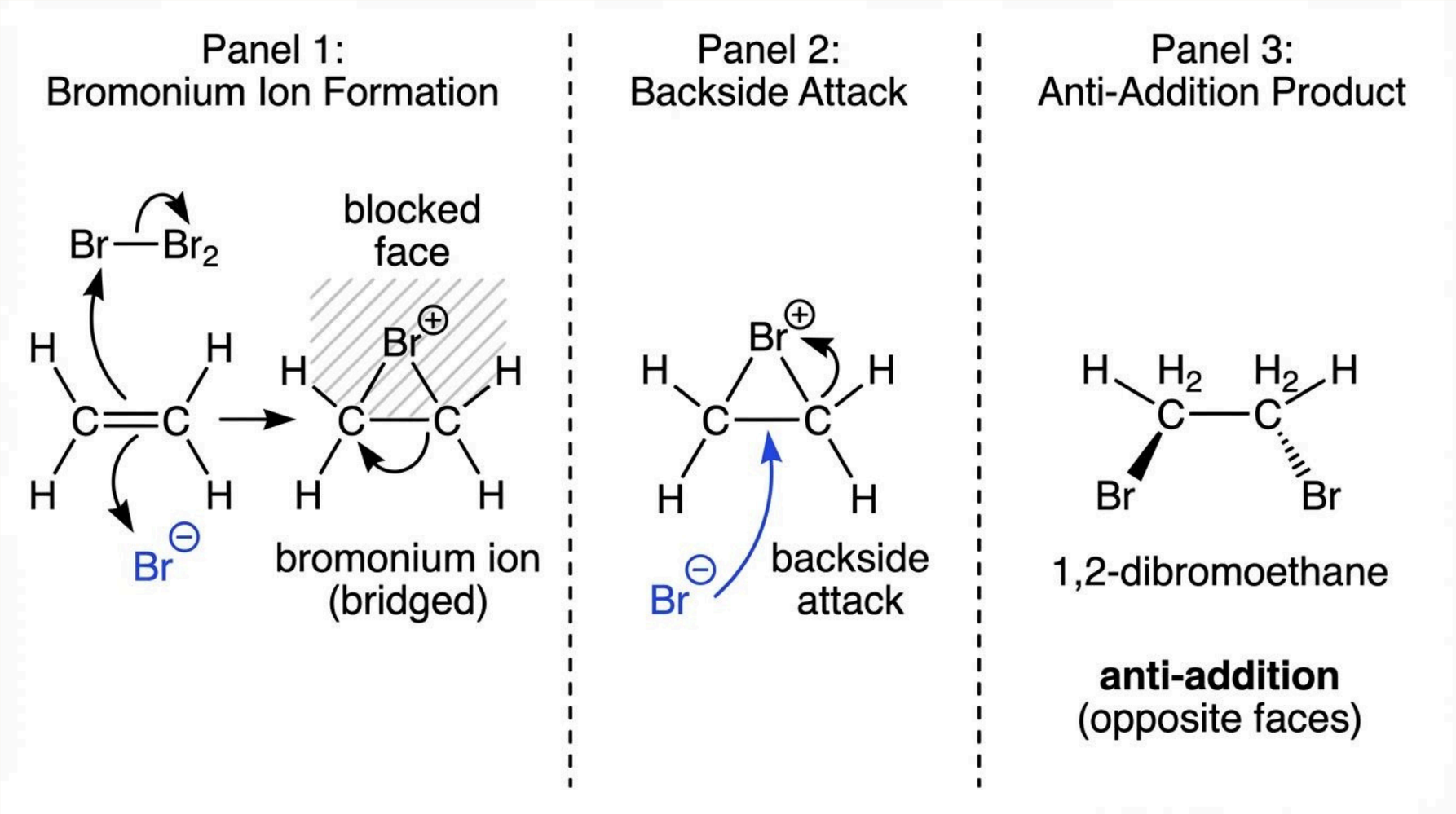


Used in petroleum processing, organic synthesis and food fats.

Halogenation of Alkenes

$CH_2=CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$

1,2-Dibromoethane



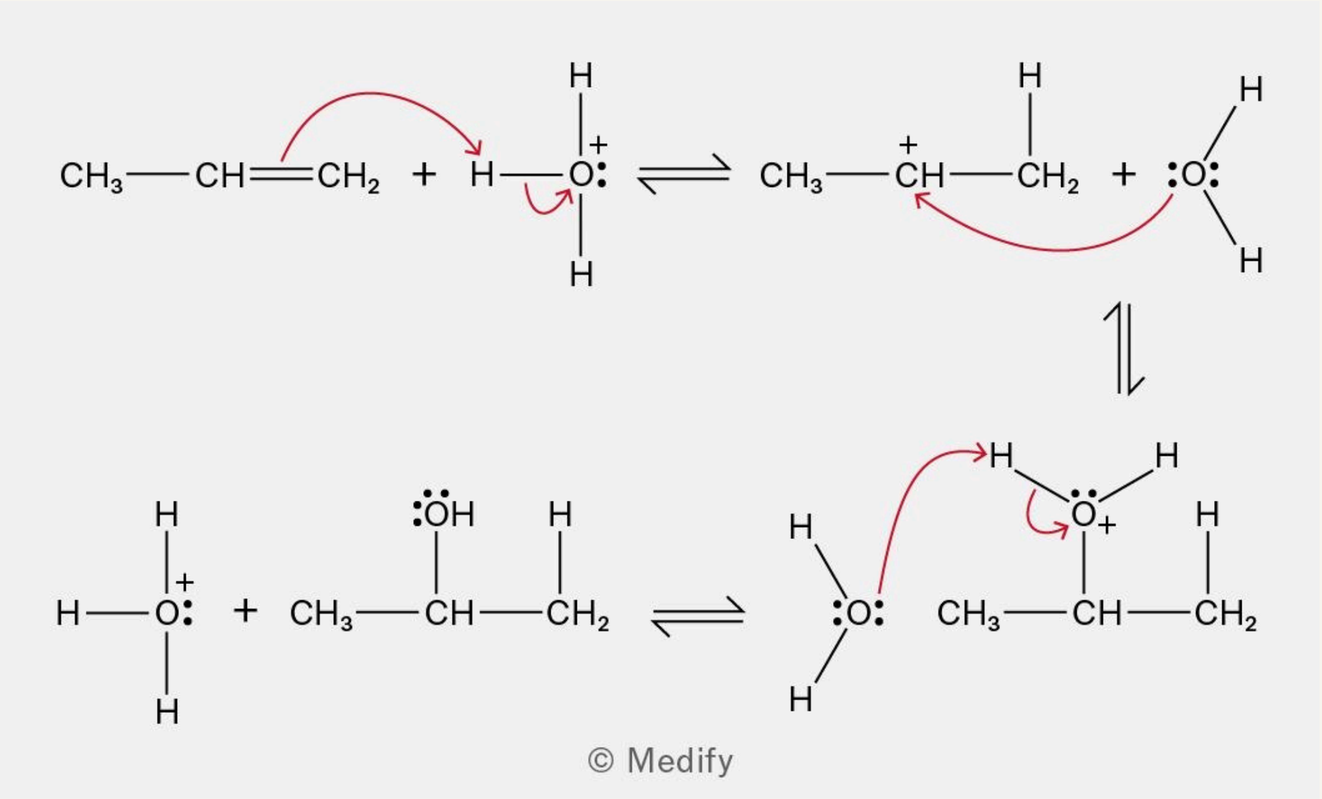
- Addition of a halogen molecule to C=C
- 1. The double bond polarizes Br_2
- 2. A cyclic bromonium ion forms
- 3. Bromide attacks from the opposite side
- 4. A vicinal dibromide results

Hydration of Alkenes

$CH_3CH=CH_2 + H_2O \xrightarrow{H^+} CH_3CH(OH)CH_3$

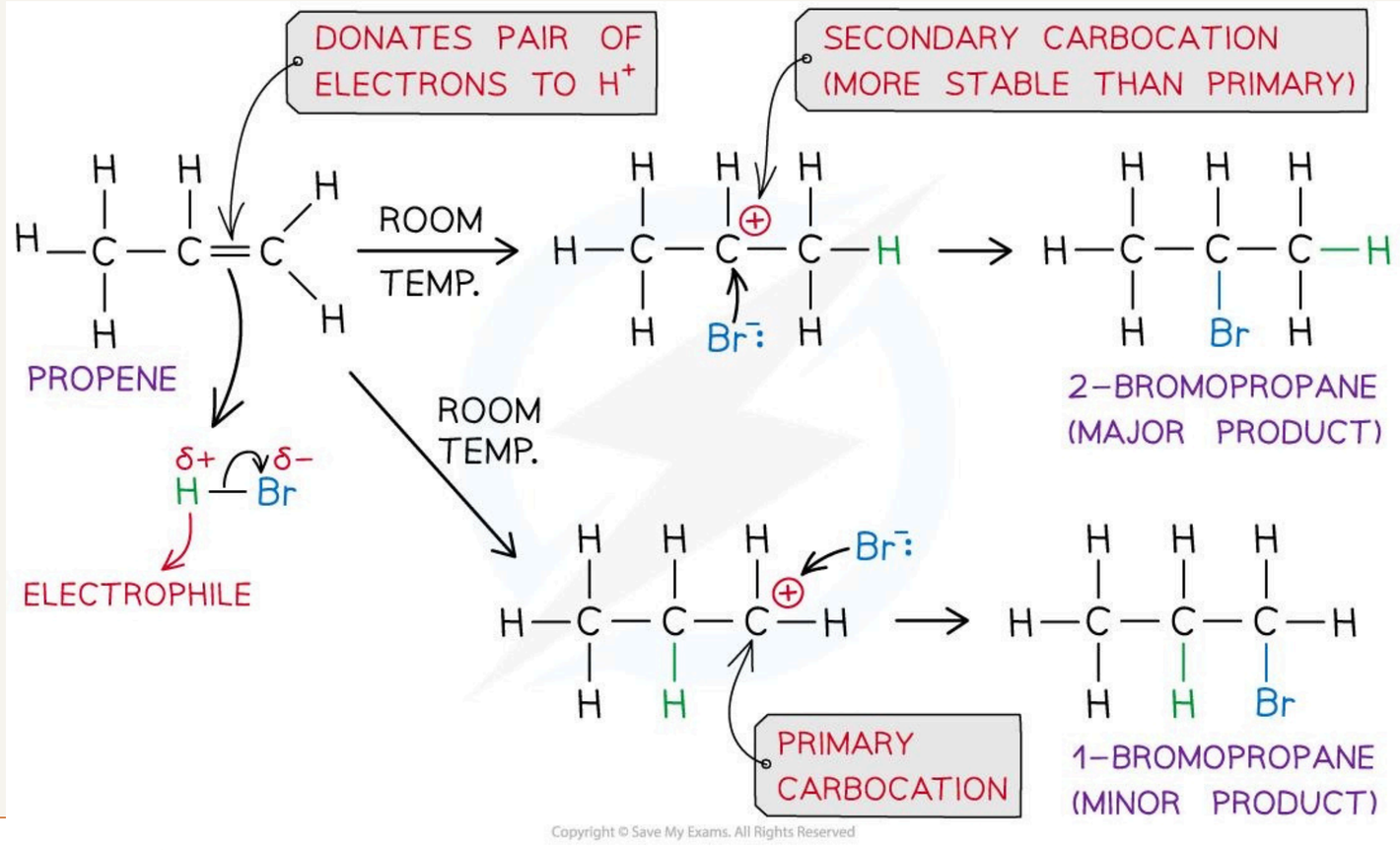
Product: propan-2-ol

- Addition of water gives an alcohol, with an acid catalyst
- Mechanism: protonation of the double bond, carbocation formation, attack by water, deprotonation
- Usually follows Markovnikov’s rule
- Carbocation rearrangements are possible



Electrophilic Addition Mechanism

- An electrophile is an electron-deficient species that accepts an electron pair
- The π bond is electron-rich, so the alkene acts as a nucleophile
- Propene + HBr: major product 2-bromopropane



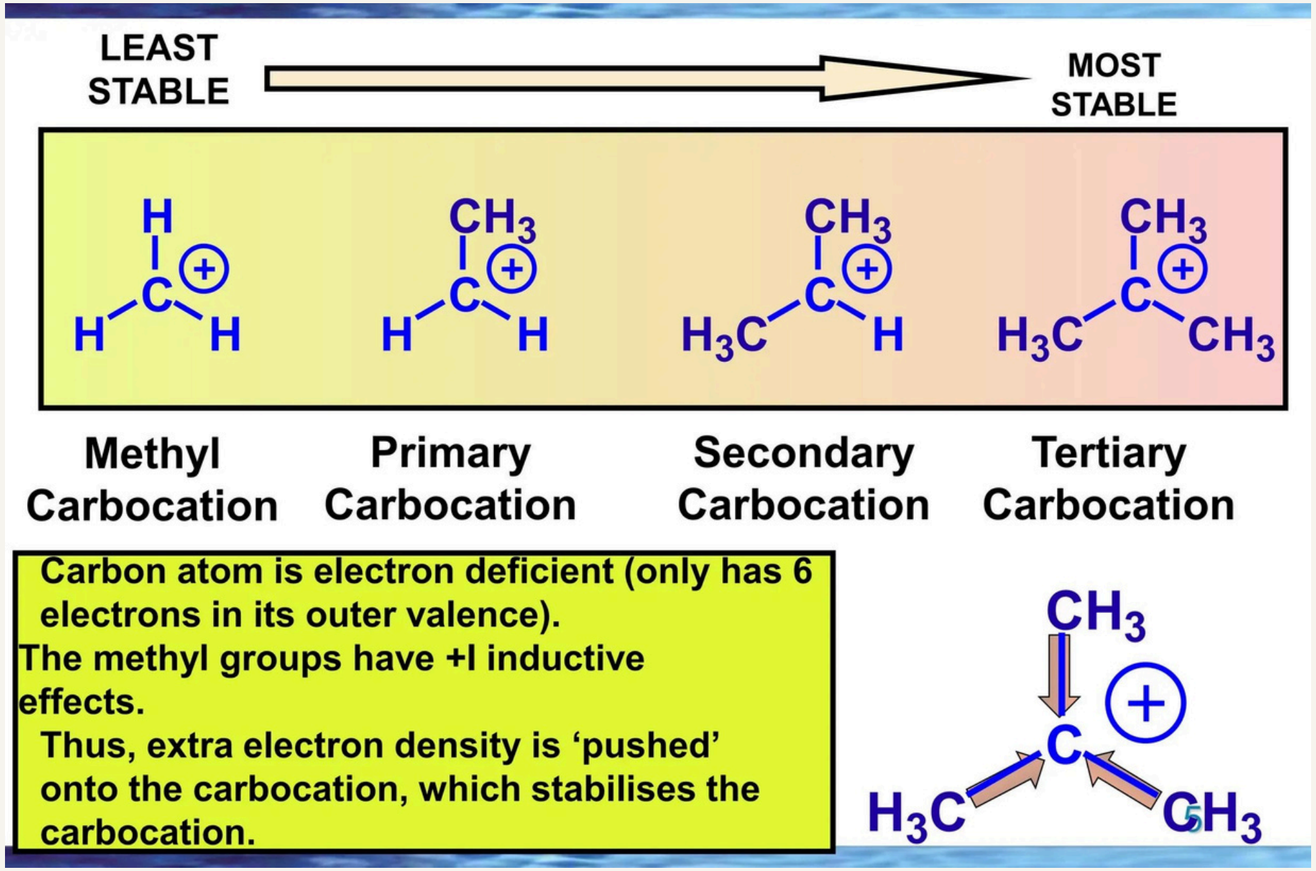
Step 1. Electrophilic attack

$CH_3CH{=}CH_2 + H^+ \rightarrow CH_3CH^+CH_3$

Step 2. Nucleophilic attack

$CH_3CH^+CH_3 + Br^- \rightarrow CH_3CHBrCH_3$

Carbocation Stability



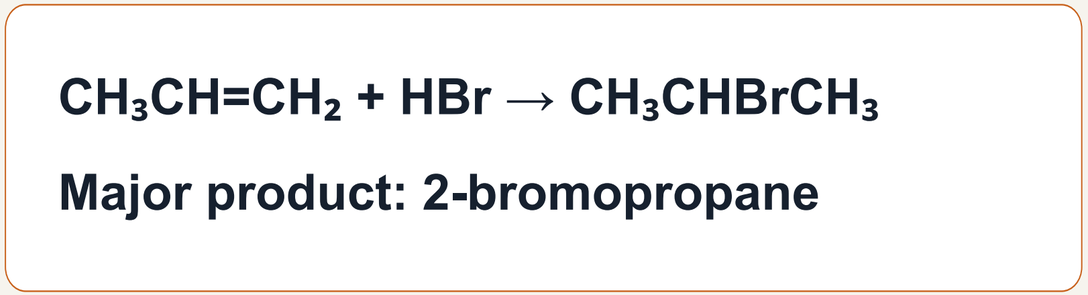
Stability order:

$3° > 2° > 1° > CH_3^+$

- Carbocations: positively charged carbon with an incomplete octet
- Stability controls the orientation of addition
- Stabilizing factors: inductive effects of alkyl groups, hyperconjugation, resonance, electron-donating substituents
- A 2° cation beats a 1° cation: two alkyl groups stabilize the charge

Markovnikov’s Rule

- Predicts orientation of HX addition to an unsymmetrical alkene under ionic conditions
- H adds to the C=C carbon with more hydrogens; the halogen goes to the more substituted carbon
- Reason: the more stable secondary carbocation forms



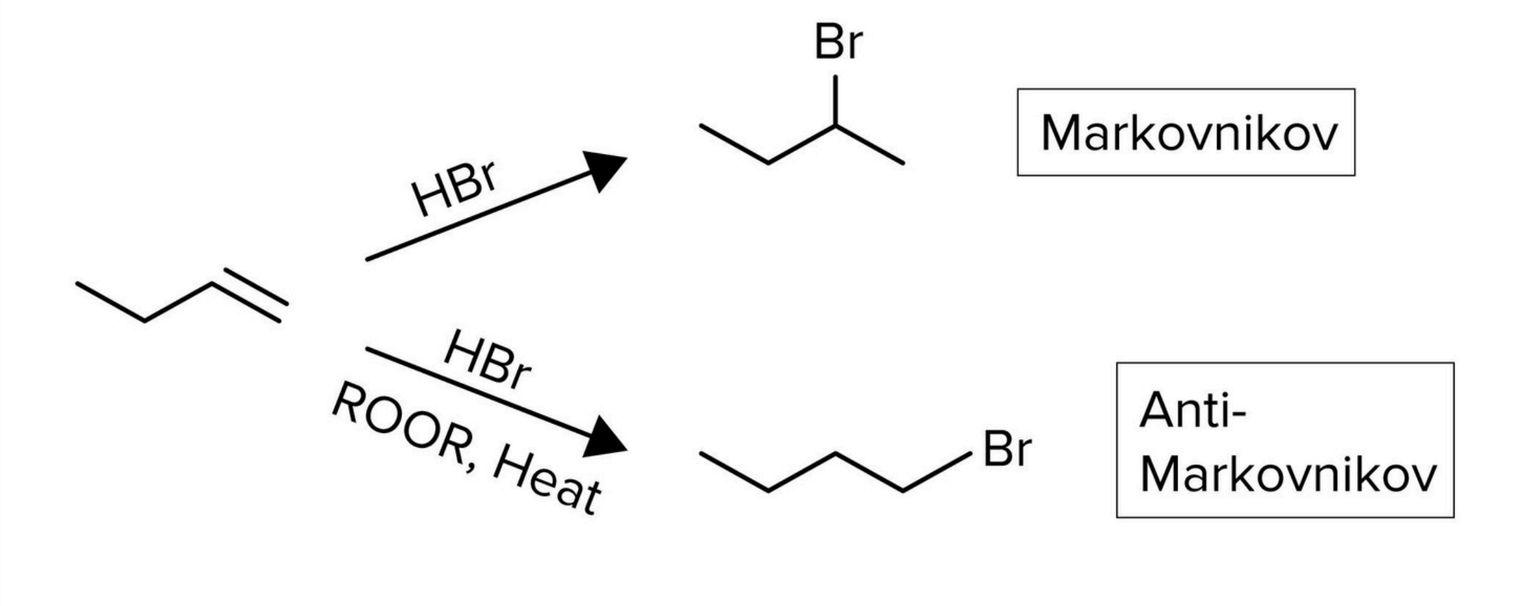
Kharasch Effect (Peroxide Effect)

- HBr adds to an unsymmetrical alkene in the presence of peroxides
- Free-radical mechanism, not ionic
- Anti-Markovnikov orientation
- Needs radical initiation
- Characteristic of HBr under suitable peroxide conditions

$RCH{=}CH_2 + HBr \xrightarrow{ROOR} RCH_2CH_2Br$

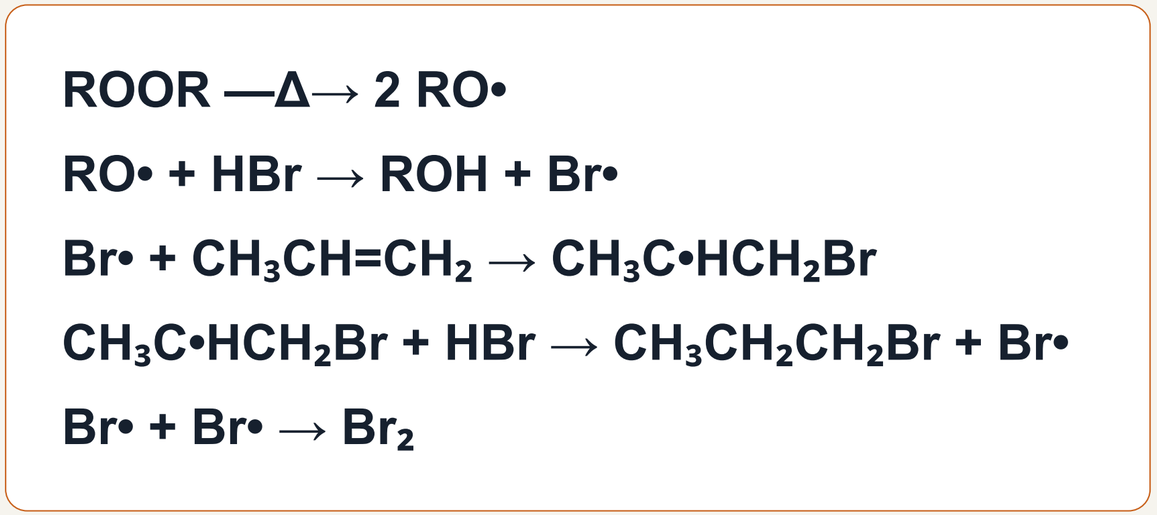
$CH_3CH{=}CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$

Product: 1-bromopropane



Kharasch Effect: Free-Radical Mechanism

- Initiation: peroxide decomposes, RO• abstracts H from HBr to give Br•
- Propagation: Br• adds to propene, then the radical abstracts H from HBr and regenerates Br•
- Termination: radicals combine to non-radical products
- Br• attacks the terminal carbon, giving the more stable secondary radical



Markovnikov vs Kharasch

Property	Markovnikov addition	Kharasch effect
Mechanism	Ionic	Free-radical
Conditions	HBr, no initiator	HBr with peroxide
Intermediate	Carbocation	Carbon radical
Bromine goes to	More substituted carbon	Less substituted carbon
Propene product	2-Bromopropane	1-Bromopropane
Regioselectivity	Markovnikov	Anti-Markovnikov

Changing conditions changes the mechanism and the major product.

Oxidation, Polymerization, Applications

$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \rightarrow 3HOCH_2CH_2OH + 2MnO_2 + 2KOH$$

$$nCH_2{=}CH_2 \rightarrow [{-}CH_2{-}CH_2{-}]_n$$

- Oxidation: $KMnO_4$ under mild conditions gives vicinal diols
- Polymerization: many alkene molecules form a polymer chain
- Polyethylene and polypropylene
- Alcohols and solvents; synthetic rubber
- Pharmaceutical intermediates; packaging and plastics



Conclusion

- 1. Alkenes readily undergo addition because of the reactive π bond
- 2. Electrophilic addition proceeds via carbocations
- 3. Markovnikov’s rule predicts the major product of ionic hydrohalogenation
- 4. Carbocation stability controls regioselectivity
- 5. The Kharasch effect is a free-radical chain mechanism
- 6. With peroxides, HBr gives anti-Markovnikov products
- 7. Alkene chemistry underpins polymers, solvents and industrial chemicals

References: McMurry; Clayden, Greeves, Warren; Solomons et al.; OpenStax.