Dehydro halogenation of alkyl halides

1,2-Elimination

What is Dehydrohalogenation?

- Dehydrohalogenation is a type of elimination reaction where an alkyl halide ($R–CH_2–CHX–R'$) loses a hydrogen atom (H) and a halogen atom (X), usually from adjacent carbon atoms, resulting in the formation of an alkene.

General reaction:

$$R–CH_2–CHX–R' \rightarrow R–CH=CH–R' + HX$$

- Requires a **base**, such as OH^- or an alkoxide ion
- Produces an alkene and a hydrogen halide (HX)

1,2-Elimination (β-Elimination)

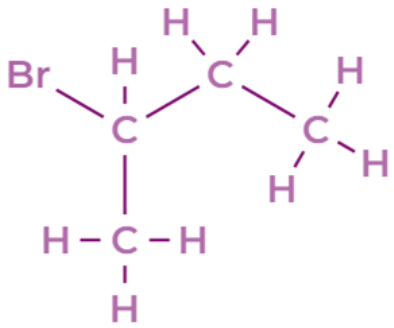
- This is called 1,2-elimination or β-elimination because:
  - The halogen (X) is removed from the α-carbon (carbon bearing the halogen)
  - The hydrogen (H) is removed from the β-carbon (adjacent to the α-carbon)
  - A double bond forms between the α- and β-carbons

Example of 1,2-Elimination

Let's consider **2-bromobutane** reacting under basic conditions:

Structure of 2-bromobutane:

- **$CH_3–CHBr–CH_2–CH_3$**



Reaction Conditions

- Under heat and strong base (e.g., KOH in ethanol), the following occurs:
  - The Br atom on carbon-2 acts as the leaving group.
  - One of the β-hydrogens is abstracted from carbon-3.
  - A double bond forms between carbon-2 and carbon-3.

Resulting Product

$CH_3–CH=CH–CH_3 + HBr$

- The product is **but-2-ene**, a typical result of a 1,2-elimination process.
- Note: There can be stereoisomers in the products (*cis* and *trans* forms), especially in symmetrical alkenes.

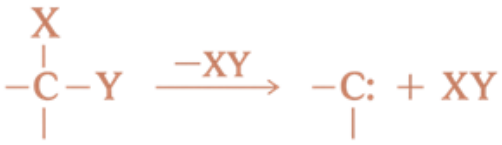
Types of 1,2-Elimination Mechanisms

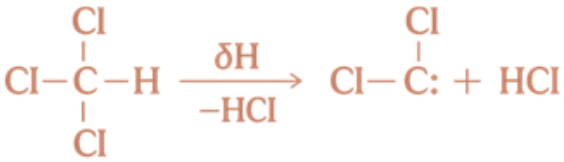
- 1,2-Elimination can proceed via two principal mechanistic pathways:
  - **A. E2 Mechanism** (Bimolecular Elimination)
  - **B. E1 Mechanism** (Unimolecular Elimination)

Why It's an Elimination

- Unlike substitution (where one group replaces another), elimination removes two atoms/groups entirely, forming a π-bond.
- The reaction reduces saturation (alkane → alkene)

Key Points of 1,2-Elimination





- Requires a base to abstract the β-hydrogen
- The halogen leaves as a leaving group
- Alkene is formed from the remaining carbons
- It's called β-elimination because the hydrogen is on the β-carbon
- Competes with substitution reactions under similar conditions

Regioselectivity and Multiple Products

- When more than one β-hydrogen is available, multiple alkenes can form.
- Their distribution depends on:
  - **Zaitsev's Rule**: The more substituted (stable) alkene is favored.
  - **Hofmann's Rule**: The less substituted alkene is favored when bulky bases are used.

General Conditions That Affect Elimination

- **Substrate**: Tertiary > secondary > primary (in terms of ease of elimination)
- **Base strength**: Strong base favors E2; weak base + heat favors E1

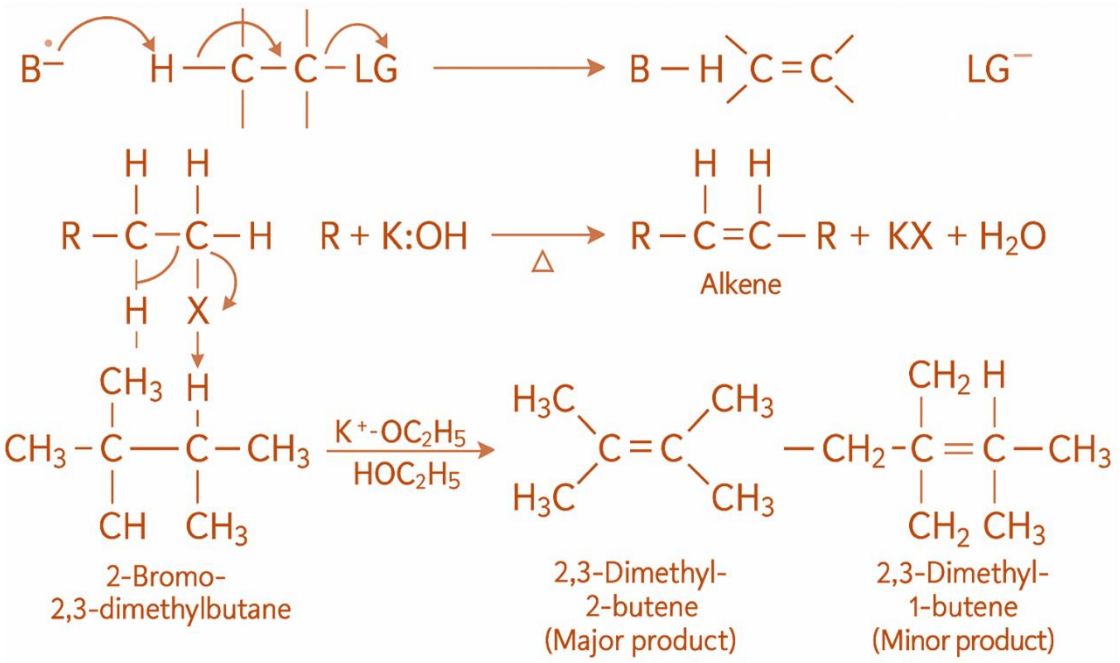
- **Leaving group**: Better leaving group ($I^- > Br^- > Cl^-$) favors elimination
- **Solvent and temperature**: Polar protic solvents and heat favor E1; aprotic + strong base favors E2

Kinetics of the E2 Mechanism

General Reaction:

Alkyl halide + strong base → alkene + HX

Example:



$CH_3CH_2CHBrCH_3 + OEt^- \rightarrow CH_3CH{=}CHCH_3 + EtOH + Br^-$

Rate Law (E2):

Rate = k [Alkyl Halide][Base]

- **Second-order overall**: The reaction rate depends on the concentration of two reactants.
- This reflects a single-step, concerted mechanism (both the base and the substrate are involved in the transition state).

Implications of the Rate Law:

- Doubling the concentration of the base doubles the rate.
- Doubling the alkyl halide concentration also doubles the rate.
- Changing the solvent or temperature can affect the rate, but concentration changes are directly reflected in the speed of reaction.

Transition State (E2):

- The reaction occurs through a single transition state where:

- The base begins to abstract the β-hydrogen,
- The π-bond begins to form between α and β carbons,
- The leaving group (X^-) starts to depart from the α-carbon.

- All of this happens simultaneously (concerted).

Kinetics of the E1 Mechanism

General Reaction:

Alkyl halide → carbocation intermediate → alkene

Example:

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_2C{=}CH_2 + HBr + H_2O$$

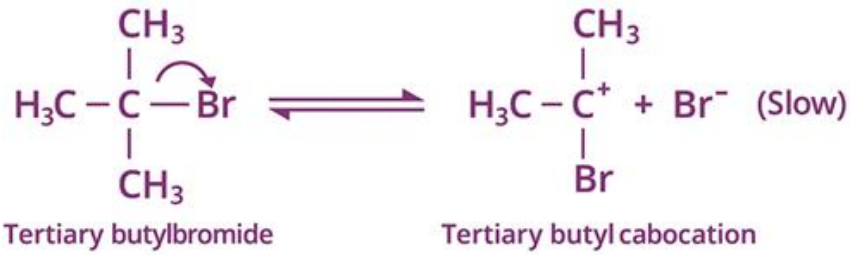
Rate Law (E1):

Rate = k [Alkyl Halide]

- **First-order overall**: The rate depends only on the concentration of the substrate (the alkyl halide).
- The base does not appear in the rate-determining step.

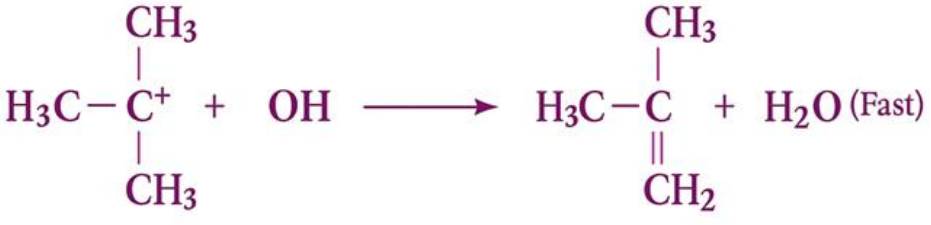
Why First-Order?

- The E1 mechanism occurs in **two steps**:
  1. **Ionization**: The halide leaves, forming a carbocation. This is the slow, rate-determining step.



Tertiary butylbromide — Tertiary butyl cabocation

  2. **Deprotonation**: A base abstracts the β-hydrogen, forming the alkene. This is a fast step.

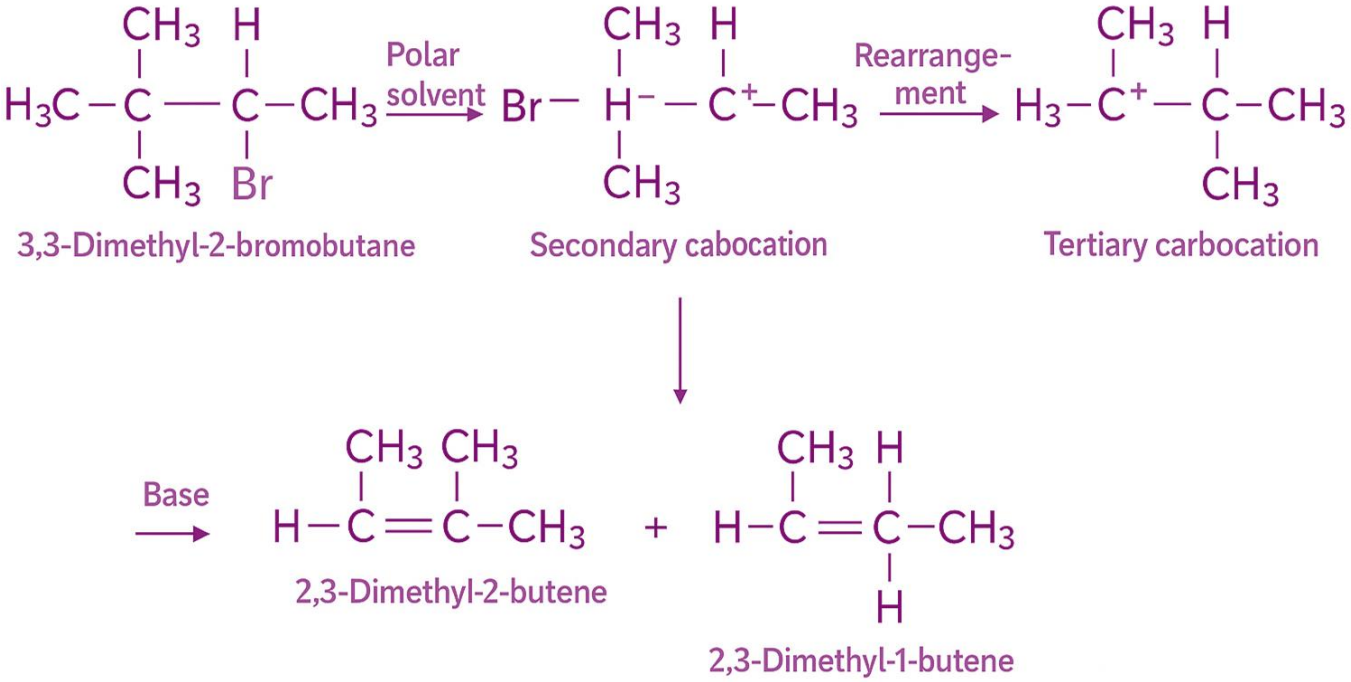


Tertiary butyl carbocation — Isobutylene

- Since only the first step (formation of the carbocation) determines the rate, the base plays **no role** in the kinetics.

Transition State (E1):

- The transition state involves only the departure of the leaving group (X^-) and formation of the carbocation.
- The elimination of the β-H occurs after the rate-limiting step.



3,3-Dimethyl-2-bromobutane — Secondary cabocation — Tertiary carbocation

E2 Mechanism (Elimination Bimolecular)

Overview of E2 Mechanism

- The E2 mechanism (Elimination, bimolecular) is a concerted reaction in which:
  - a base removes a β-hydrogen,
  - a π-bond (double bond) forms between the α- and β-carbons, and
  - a leaving group (halide) departs —all in one single step.
- This is a fundamental reaction in organic chemistry, widely used for the synthesis of alkenes from alkyl halides, especially when strong bases are present.

General Form of the E2 Reaction

- Let's consider a generic alkyl halide:

$$Base^- + R–CH_2–CH_2–X \rightarrow R–CH=CH_2 + Base–H + X^-$$

  - R = alkyl group
  - X = leaving group (typically Br^-, Cl^-, I^-)
  - $Base^-$ = strong base (e.g., ^-OH, ^-OR, $^-NH_2$, tert-butoxide)
  - Product = alkene

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