

FUNDAMENTAL CONCEPTS IN REACTION MECHANISMS

Fission of a Covalent Bond

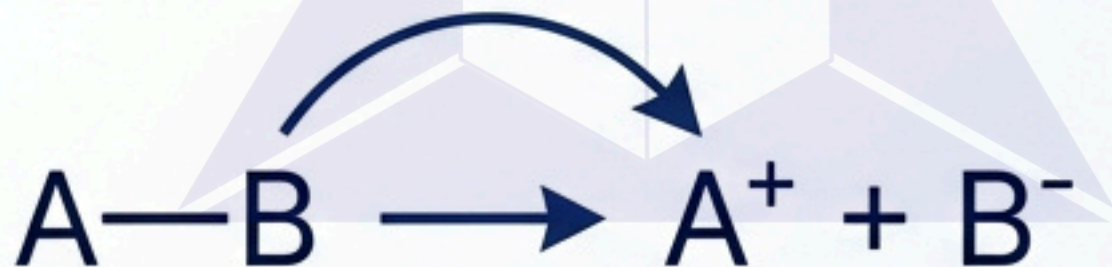
Understanding Cleavage Pathways & Reactive Intermediates

Master organic reaction pathways by decoding how bonds break and the transient species they leave behind.

Two Pathways of Covalent Fission

Heterolytic Cleavage [Unequal Split]

The bond breaks unsymmetrically. One atom takes both shared electrons from the covalent bond.



Result: Forms charged ions (cations and anions).

Homolytic Cleavage [Equal Split]

The bond breaks symmetrically. Each atom takes away one of the shared electrons.

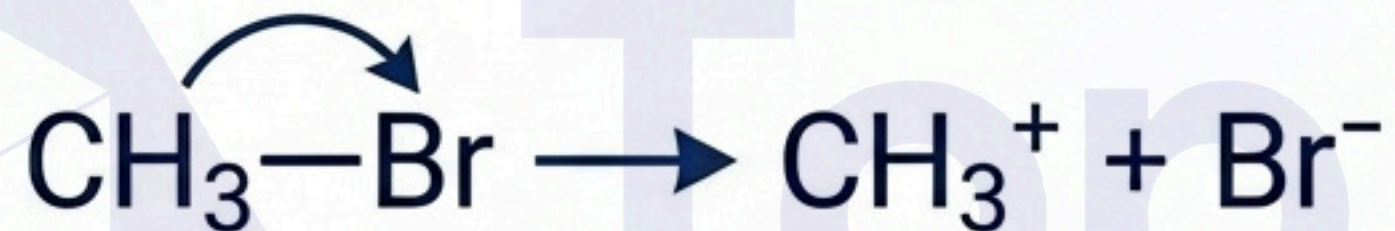


Result: Forms neutral free radicals.

Heterolytic Cleavage: Creating Charged Intermediates

The Electron Shift

Driven by differences in electronegativity. The more electronegative atom retains the entire electron pair.



[Carbon Loses Electrons]

Forms a Carbocation (CH_3^+).

- Geometry: sp^2 hybridized, trigonal planar.
- Features: Empty p orbital, only 6 valence electrons, highly unstable and reactive.

[Carbon Gains Electrons]

Forms a Carbanion (CH_3^-).

- Features: Carbon holds an unshared pair of electrons, 8 valence electrons (complete octet), highly reactive intermediate.



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$$E=mc^2$$



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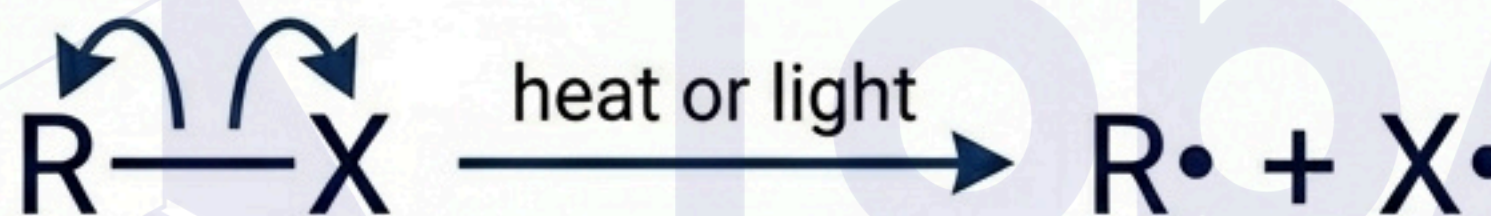
Homolytic Cleavage: Forging Free Radicals

[Requires Heat]

[Requires Light (hv)]

[Requires Peroxides]

In a homolytic fission, the shared pair of electrons is divided equally. This requires specific environmental energy conditions to initiate.



The Reactive Intermediate: Free Radical

Alkyl free radicals are neutral chemical species carrying an unpaired electron.

- Similar to carbocations, they are sp^2 hybridized (planar) and are highly reactive transient species seeking to pair their lone electron.
- Stability is determined by the dispersal of this electron deficiency through neighboring alkyl groups.

Profiling Reactive Intermediates

	Carbocation (C ⁺)	Carbanion (C ⁻)	Free Radical (C•)
Cleavage Origin	Heterolytic (C loses e ⁻)	Heterolytic (C gains e ⁻)	Homolytic
Valence Electrons	6 electrons (electron deficient)	8 electrons (octet complete)	7 electrons (unpaired e ⁻)
Hybridization & Shape	sp ² , Trigonal Planar	Often sp ³ , Pyramidal	sp ² , Planar (usually)
Stability Trend	3° > 2° > 1° > methyl	methyl > 1° > 2° > 3°	3° > 2° > 1° > methyl
Stabilizing Factors	+I (Inductive), Hyperconjugation	-I (Inductive) effect	Hyperconjugation

Note how Carbocations and Free Radicals share the exact same stability trend due to both being electron-deficient species seeking electron dispersal.

Key Takeaways

- ✓ **Arrow Notation is Crucial**
 - ✓ Full curved arrows denote heterolytic cleavage (movement of an electron pair).
 - ✓ Half-headed (fish-hook) arrows denote homolytic cleavage (movement of a single electron).
- ✓ **Heterolytic Fission = Ions**
 - ✓ Creates electron-deficient Carbocations ($6e^-$, sp^2 , planar) or electron-rich Carbanions ($8e^-$).
- ✓ **Homolytic Fission = Radicals**
 - ✓ Triggered by heat, light, or peroxides, resulting in neutral, unpaired-electron species called Free Radicals ($7e^-$).
- ✓ **Stability Trends Rule Reactions**
 - ✓ Because Carbocations and Free Radicals both need electrons, their stability increases with substitution ($3^\circ > 2^\circ > 1^\circ$). Carbanions are the exact reverse.



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