Free Radicals: Structure, Stability, and Bond Dissociation Energy — Study Guide

In this guide we cover everything you need to understand about free radicals before tackling the radical halogenation mechanism. We start with what a radical is at the electronic level, how homolytic bond cleavage generates them, why some radicals are more stable than others, and how Bond Dissociation Energy (BDE) connects all of it. This is the foundation for predicting which C–H bonds react and why. Drawing on Clayden's Organic Chemistry, Wade's Organic Chemistry, McMurry's Organic Chemistry, and Chemistry LibreTexts.

1. What is a Free Radical? Structure and Electronic Nature

A free radical is any species that contains an unpaired electron. In organic chemistry, carbon-centered radicals are the most important — these are species where one carbon atom bears an unpaired electron rather than a full electron pair.

Free radicals are fundamentally different from the ionic intermediates (carbocations and carbanions) you have already studied:

Intermediate	Electrons at Carbon	Charge	Geometry
Carbocation	6 electrons (empty p-orbital)	Positive (+)	sp^2, trigonal planar
Carbanion	8 electrons (lone pair)	Negative (−)	sp^3, tetrahedral
Carbon radical	7 electrons (one unpaired)	Neutral (0)	sp^3 or sp^2 (near-planar)

Carbon radicals are drawn with a dot (•) to represent the unpaired electron: CH_3• (methyl radical), $(CH_3)_3C$• (tert-butyl radical). The dot is not just a drawing convention — it tells you that this species will react very rapidly with almost anything that can provide an electron or a bond partner.

How Are Radicals Formed?

Radicals are generated by homolytic bond cleavage, which requires an input of energy. The two most common energy sources in laboratory radical reactions are:

- Ultraviolet (UV) light or visible light (photochemical initiation, abbreviated hv)
- Heat (thermal initiation, typically >100°C for halogen molecules)
- Radical initiators such as ROOR (peroxides) that fragment homolytically at moderate temperatures

> Radical reactions are fundamentally different from ionic reactions in that they require an external energy source to get started. They do not simply occur when two reagents are mixed at room temperature in the dark — this is why methane and Cl_2 can be stored together with no reaction until light or heat is applied.

Radical vs Ionic Chemistry: The Big Distinction

Feature	Ionic Chemistry (SN1, SN2, E1, E2, Electrophilic Addition)
Bond breaking	Heterolytic — both electrons go to one atom

Intermediates	Carbocations, carbanions, halonium ions
Driving force	Charge stabilization, nucleophile/electrophile interaction
Initiation	No initiation needed — reagents react directly
Chain reaction?	No
Curved arrows	Two-headed arrows (pairs of electrons)

2. Homolytic vs Heterolytic Bond Cleavage

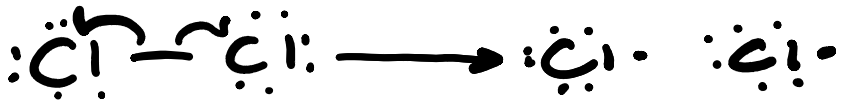
When a covalent bond breaks, the two electrons that made up that bond must go somewhere. There are exactly two possibilities, and they lead to completely different types of chemistry:

Type of Cleavage	What Happens
Heterolytic cleavage	Both electrons go to the more electronegative atom. One atom becomes electron-rich (anion or neutral nucleophile); the other becomes electron-poor (cation or electrophile).
Homolytic cleavage	One electron goes to each atom. Both atoms end up with an unpaired electron and are neutral (or carry radical character).

Visualizing Homolytic Cleavage

The key halogen bond that initiates radical halogenation is the X–X bond in Cl_2 or Br_2. When this bond undergoes homolytic cleavage:

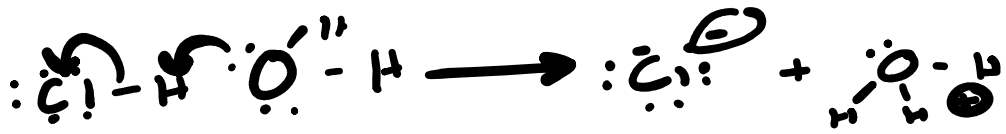
Cl–Cl → Cl• + Cl• (homolytic cleavage; each Cl gets one electron)



Each chlorine atom now has seven valence electrons and one unpaired electron. This chlorine radical is highly reactive and will immediately seek to form a bond to stabilize itself, initiating the chain reaction.

Contrast this with what happens in ionic reactions such as HCl dissolving in water:

H–Cl + H_2O → H_3O^+ + Cl^- (heterolytic cleavage; both electrons go to Cl)



Curved arrow notation: In radical mechanisms, always use fishhook (half-headed) arrows to show the movement of single electrons. Using full double-headed arrows in a radical mechanism is a significant error. One fishhook arrow per electron moving.

When Does Homolytic Cleavage Occur?

Homolytic cleavage is favored when:

- Bond polarity is low (nonpolar or weakly polar bonds like Cl–Cl, Br–Br, or C–C). There is no reason for both electrons to go to one atom if the atoms have similar electronegativities.
- External energy is supplied (light or heat). Homolytic cleavage is always endothermic (bond breaking requires energy). The energy supplied by a photon or heat is what drives the initiation step.
- The radicals formed are reasonably stable. The more stable the radicals produced, the lower the activation energy for cleavage.

3. Radical Stability: The Stability Order and Why It Exists

Just as carbocation stability is fundamental to understanding SN1, E1, and electrophilic addition, radical stability is fundamental to understanding radical halogenation. The more stable the radical intermediate, the more easily it forms, and the lower the activation energy for the step that produces it.

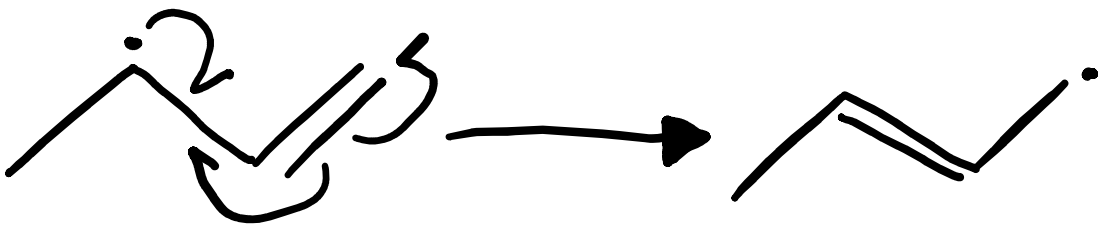
The Radical Stability Order

Tertiary (3°) > Secondary (2°) > Primary (1°) > Methyl

Radical Type	Example
Methyl	CH_3•
Primary (1°)	CH_3CH_2•
Secondary (2°)	$(CH_3)_2CH$•
Tertiary (3°)	$(CH_3)_3C$•
Allylic (next to C=C)	CH_2=$CHCH_2$•
Benzylic (next to ring)	$C_6H_5CH_2$•

Notice that this is the same trend as carbocation stability, but for a different reason. Carbocations are stabilized because alkyl groups donate electron density into the empty p-orbital (hyperconjugation and inductive effects). Radicals are stabilized by the same interactions, but now the orbital being stabilized contains one electron rather than being empty.

Why adjacent pi bonds stabilize the radical:



Why Are More-Substituted Radicals More Stable?

Reason 1: Hyperconjugation

Alkyl groups adjacent to the radical center can donate electron density through hyperconjugation — the partial overlap of adjacent C–H and C–C σ bonds with the half-filled orbital on the radical carbon. Each additional alkyl group provides more of this stabilizing overlap. A tertiary radical has three alkyl groups doing this; a primary radical has only one.

Reason 2: Inductive Electron Donation

Alkyl groups are weakly electron-donating through the σ bond framework (inductive effect). This slight donation of electron density toward the radical center provides additional stabilization. More alkyl groups = greater inductive stabilization.

> The stability difference between radical types is smaller than for carbocations. A tertiary radical is only about 3–4 kcal/mol more stable than a primary radical (corresponding to the BDE differences in the table above). This matters enormously for selectivity, as we will see in Section 8.

Radical Geometry

Carbon radicals have a geometry that is close to but not quite planar. The radical carbon is approximately sp^2 hybridized, similar to a carbocation, with the unpaired electron in a p-type orbital perpendicular to the three substituents. However, the radical center inverts rapidly (the ‘umbrella flip’), so radicals do NOT lead to retention of configuration at the radical center. If a radical is formed at a stereocenter, the product is typically a racemic mixture.

4. Bond Dissociation Energy (BDE) and Its Role in Radical Reactions

Bond Dissociation Energy (BDE) is defined as the energy required to break a bond homolytically in the gas phase, producing two radicals. It is always positive (endothermic) because bond breaking always requires an input of energy.

$$A–B \rightarrow A\bullet + B\bullet \qquad \Delta H = BDE \text{ (always positive)}$$

Key BDE Values for Radical Halogenation

Bond	BDE (kcal/mol)
Cl–Cl	58
Br–Br	46
F–F	38
I–I	36
H–Cl	103
H–Br	87
1° C–H ($R–CH_3$)	~100
2° C–H (R_2CH_2)	~98–99
3° C–H (R_3CH)	~95–96
Allylic C–H	~88

Using BDE to Calculate Reaction Enthalpy

For any radical reaction step, you can calculate the enthalpy change (ΔH) using BDE values:

$$\Delta H = \Sigma BDE(\text{bonds broken}) - \Sigma BDE(\text{bonds formed})$$

Bonds broken are endothermic (+); bonds formed are exothermic (−). The sign of ΔH tells you whether the step is favorable (exothermic, $\Delta H < 0$) or unfavorable (endothermic, $\Delta H > 0$).

Worked Example — Propagation Step 1 of Chlorination of Methane:

$CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$

1. Bond broken: C–H in methane. BDE = +105 kcal/mol (endothermic, energy in).
2. Bond formed: H–Cl. BDE = −103 kcal/mol (exothermic, energy released).
3. ΔH = +105 − 103 = −2 kcal/mol. Slightly exothermic overall. The step is thermodynamically favorable.

Worked Example — Propagation Step 1 of Bromination of Methane:

$CH_4 + Br\bullet \rightarrow CH_3\bullet + HBr$

1. Bond broken: C–H in methane. BDE = +105 kcal/mol.
2. Bond formed: H–Br. BDE = −87 kcal/mol.
3. ΔH = +105 − 87 = +18 kcal/mol. Endothermic. This step is thermodynamically unfavorable for methane bromination.

This endothermicity of Step 1 in bromination is the mechanistic reason why bromination is much more selective than chlorination. An endothermic step has a later transition state that looks more like the product (the radical). Radical stability therefore matters more for bromination than for chlorination. See Section 9 for the full Hammond Postulate argument.

Quick Recap

- ✓ Radicals are neutral species with one unpaired electron — formed by homolytic bond cleavage
- ✓ Use fishhook (half-headed) arrows for radical mechanisms, never full curved arrows
- ✓ Radical stability: 3° > 2° > 1° > methyl; allylic ≈ benzylic >> 3° (resonance)
- ✓ BDE = energy to break bond homolytically; lower BDE = weaker bond = easier to break
- ✓ Use ΔH = ΣBDE(broken) − ΣBDE(formed) to assess each propagation step
- ✓ Bromination H-abstraction is endothermic; chlorination H-abstraction is exothermic — this drives selectivity
- ✗ Don’t confuse homolytic (radicals) and heterolytic (ions) cleavage
- ✗ Don’t confuse radical stability with carbocation stability — same order, different reason

References & Further Reading

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