

Organic Chemistry I

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3. Reaction of Alkanes

Homolytic Cleavage: Bonding Electrons Separate

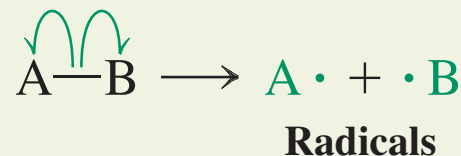
The bond breaks in such a way that the two bonding electrons divide equally between the two participating atoms or fragments. This process is called **homolytic cleavage** or **bond homolysis**.


The separation of the two bonding electrons is denoted by two *single-barbed* or “fishhook” arrows that point from the bond to each of the atoms.

The fragments that form have an unpaired electron (H^\cdot , Cl^\cdot , $^\cdot\text{CH}_3$, and $\text{CH}_3\text{CH}_2^\cdot$). When these species are composed of more than one atom, they are called **radicals**.

Because of the unpaired electron, radicals and free atoms are **very reactive** and usually **cannot be isolated**.

Homolytic Cleavage: Bonding Electrons Separate



A single-barbed arrow  shows the movement of a *single* electron.

Heterolytic Cleavage: Bonding Electrons Move as Pair

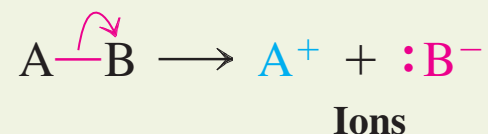
An alternative way of breaking a bond, in which the entire bonding electron pair is donated to one of the atoms. This process is **heterolytic cleavage** and results in the formation of **ions**.

Homolytic cleavage may be observed in nonpolar solvents or even in the gas phase.

In contrast, heterolytic cleavage normally occurs in polar solvents, which are capable of stabilizing ions.

Heterolytic cleavage is also restricted to situations where the electronegativities of atoms A and B and the groups attached to them stabilize positive and negative charges, respectively.

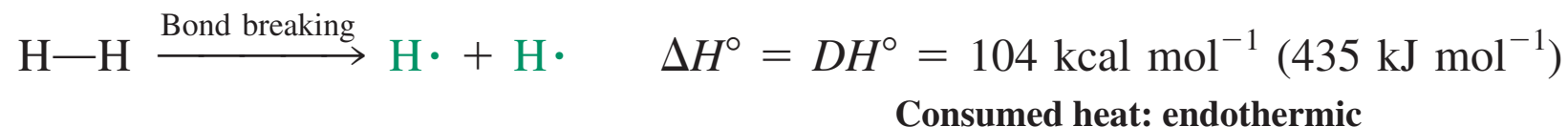
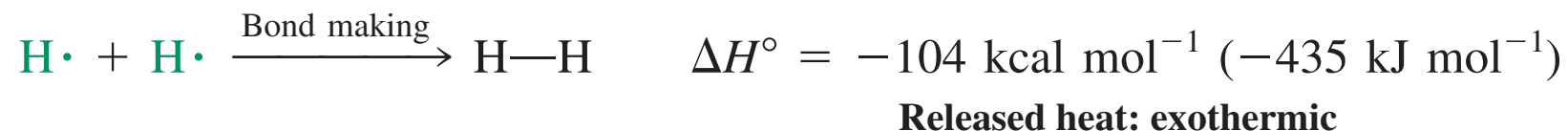
Heterolytic Cleavage: Bonding Electrons Move as Pair



A normal, double-barbed curved arrow \curvearrowright shows the movement of a *pair* of electrons.

Homolytic breaking of a bond *requires* heat—in fact, the same amount of heat that was released when the bond was made.

This energy is called **bond-dissociation energy**, DH° , and is a quantitative measure of the **bond strength**.



Dissociation energies, DH° , refer only to homolytic cleavages. They have characteristic values for the various bonds that can be formed between the elements.

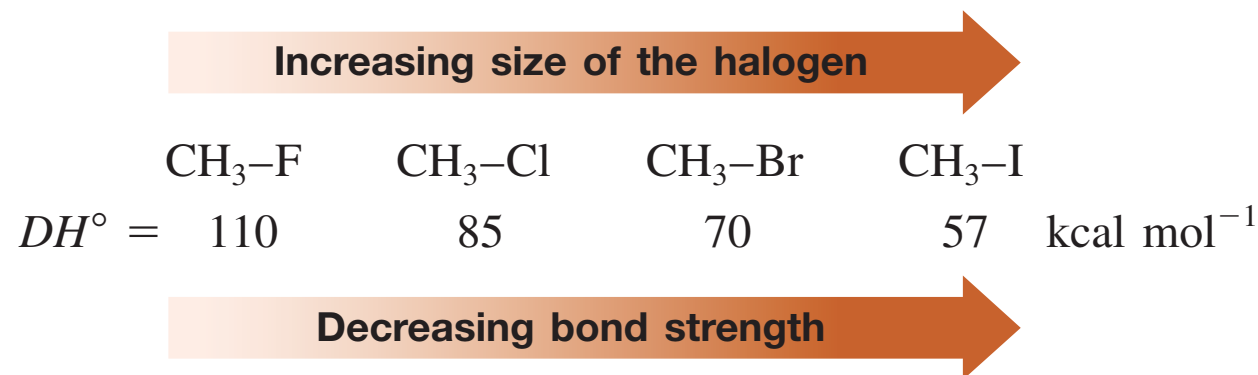
The larger the value for DH° , the stronger the corresponding bond.

Bonds are strongest when made by overlapping orbitals that are closely matched in energy and size.

For example, the strength of the bonds between hydrogen and the halogens decreases in the order $F > Cl > Br > I$, because the p orbital of the halogen contributing to the bonding becomes larger and more diffuse along the series.

Thus, the efficiency of its overlap with the relatively small $1s$ orbital on hydrogen diminishes.

A similar trend holds for bonding between the halogens and carbon.



The stability of radicals determines the C–H bond strengths



The bond energies generally decrease with the progression from methane to primary, secondary, and tertiary carbon.

C–H Bond Strength in Alkanes



Decreasing bond strength 

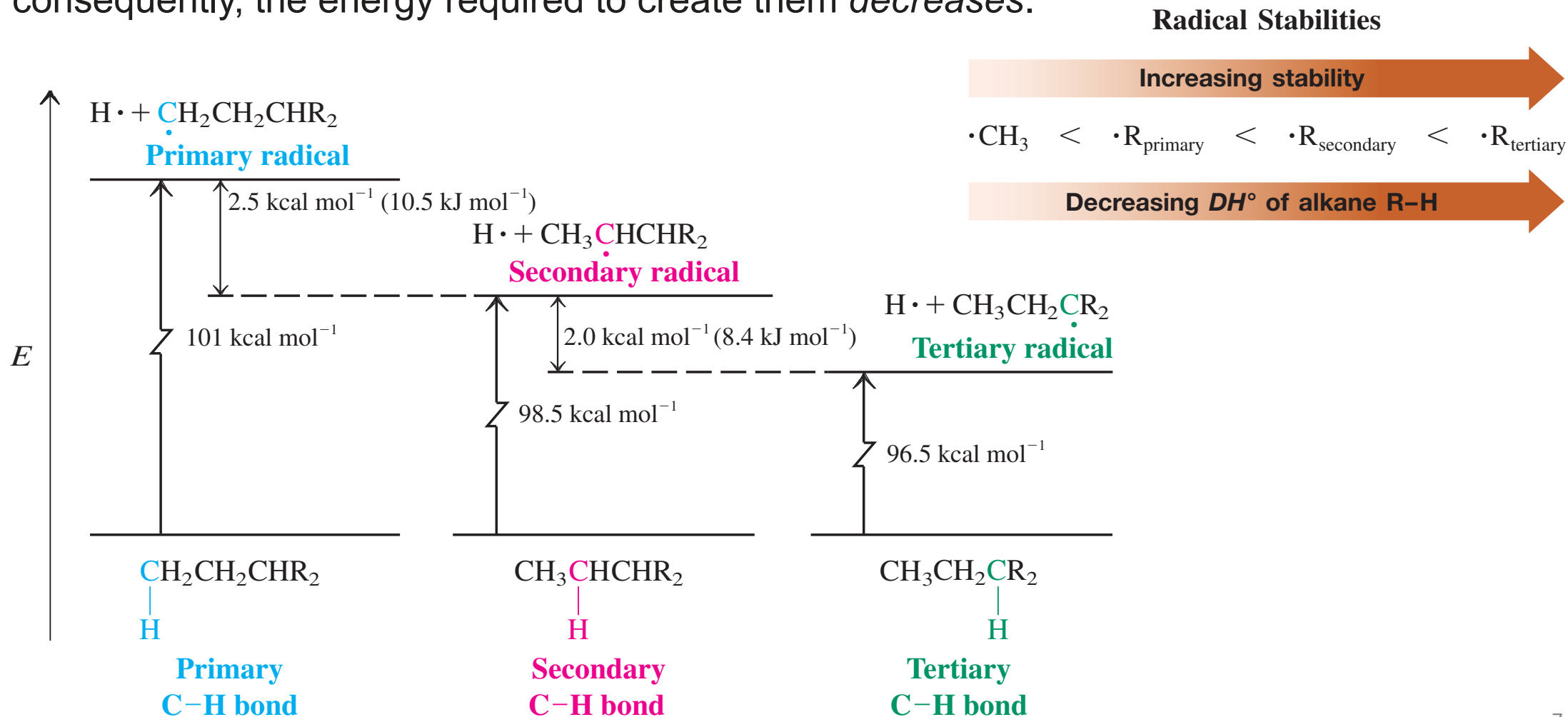
Table 3-2 Bond-Dissociation Energies for Some Alkanes

Compound	DH° [kcal mol ⁻¹ (kJ mol ⁻¹)]		Compound	DH° [kcal mol ⁻¹ (kJ mol ⁻¹)]	
CH ₃ –H	105 (439)	Decreasing DH° 	CH ₃ –CH ₃	90 (377)	Decreasing DH° 
C ₂ H ₅ –H	101 (423)		C ₂ H ₅ –CH ₃	89 (372)	
C ₃ H ₇ –H	101 (423)		C ₂ H ₅ –C ₂ H ₅	88 (368)	
(CH ₃) ₂ CHCH ₂ –H	101 (423)		(CH ₃) ₂ CH–CH ₃	88 (368)	
(CH ₃) ₂ CH–H	98.5 (412)		(CH ₃) ₃ C–CH ₃	87 (364)	
(CH ₃) ₃ C–H	96.5 (404)		(CH ₃) ₂ CH–CH(CH ₃) ₂	85.5 (358)	
		(CH ₃) ₃ C–C(CH ₃) ₃	78.5 (328)		

Note: See footnote for Table 3-1.

A similar trend is seen for C–C bonds.

The radical stability *increases* along the series from primary to secondary to tertiary; consequently, the energy required to create them *decreases*.

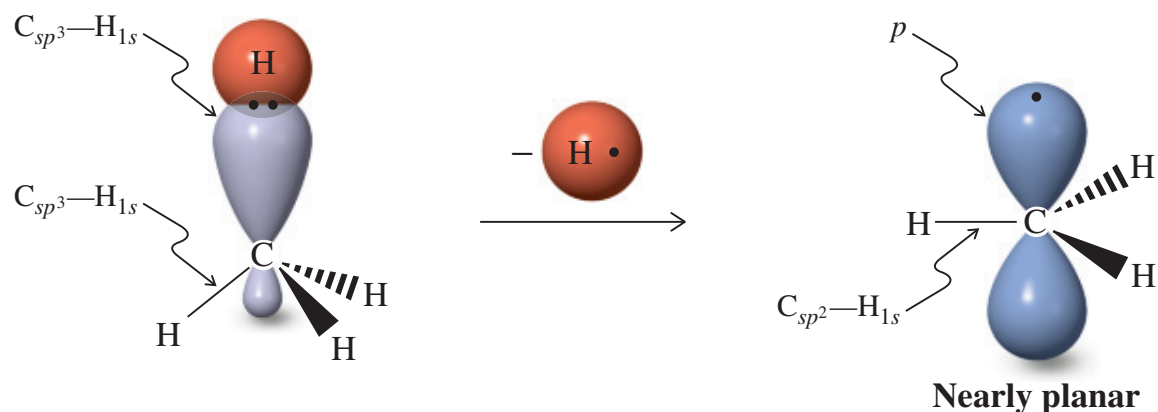


STRUCTURE OF ALKYL RADICALS: HYPERCONJUGATION

What is the reason for the ordering in stability of alkyl radicals?

The methyl radical, and probably other alkyl radicals, adopts a *nearly planar* configuration, best described by sp^2 hybridization.

The unpaired electron occupies the remaining p orbital perpendicular to the molecular plane.



The planar structures of alkyl radicals help explain their relative stabilities.

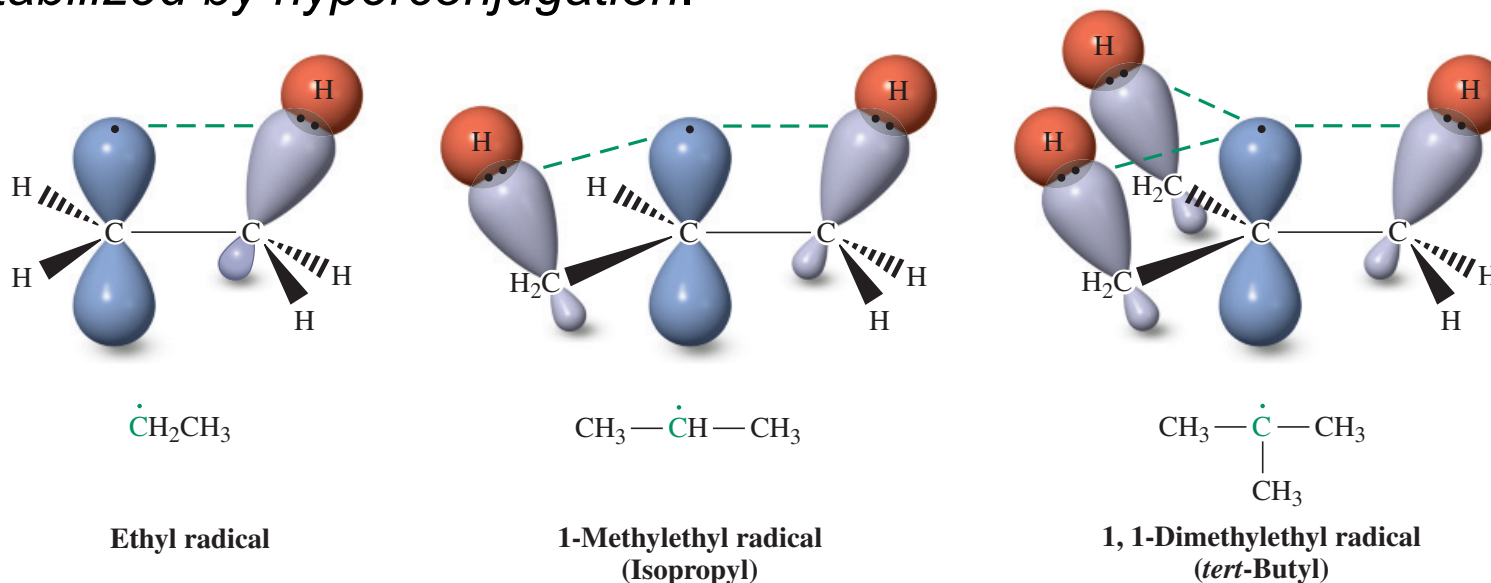
There is a conformer in the ethyl radical in which a C–H bond of the CH₃ group is aligned with and overlaps one of the lobes of the singly occupied *p* orbital on the radical center.

This arrangement allows the bonding pair of electrons in the σ orbital to delocalize into the partly empty *p* lobe, a phenomenon called **hyperconjugation**.

The interaction between a filled orbital and a singly occupied orbital has a net stabilizing effect. Both hyperconjugation and resonance are forms of electron delocalization.

They are distinguished by type of orbital: **Resonance** normally refers to π -**type** overlap of *p* orbitals, whereas **hyperconjugation** incorporates overlap with the orbitals of σ **bonds**.

Radicals are stabilized by hyperconjugation.



Each additional alkyl group increases the hyperconjugation interactions further. The order of stability of the radicals is a consequence of this effect.

The degree of stabilization arising from each hyperconjugative interaction is smaller than the stabilization of radicals by resonance

The relative stability of secondary and tertiary radicals is the greater relief of steric crowding between the substituent groups as the geometry changes from tetrahedral in the alkane to planar in the radical.

The longer bonds between carbon and large atoms reduce the steric repulsion between atoms around that carbon, diminishing its influence on bond-dissociation energies.