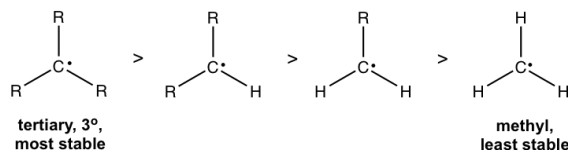


## 9.3: Stability of Alkyl Radicals

Alkyl radical is the key intermediate for halogenation reaction of alkanes, so the relative stability of radical determines the relative reactivity. Based on the energy diagram, the alkane that generate the more stable carbon radical exhibits the higher reactivity.

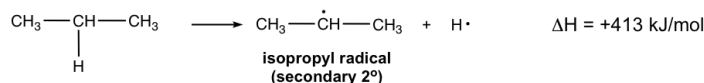
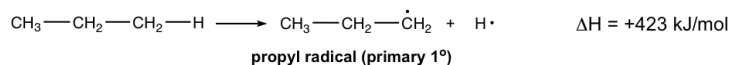
The alkyl radicals with different structures show different stabilities. Specifically, tertiary radical is most stable and the primary and methyl radicals are least stable, that follow the same trend as the stability of carbocations.



the relative stability of alkyl radicals

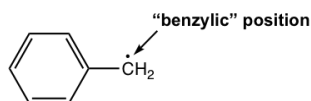
This trend can be explained by two reasonings:

- **Hyperconjugation effect** of alkyl (R) group: alkyl groups are electron-donating groups through hyperconjugation effect (refer to section 7.4), that is the electron density of C-C or C-H  $\sigma$  bond overlap with the half-filled p orbital of carbon radical. Similar to the carbocation, carbon radical is also the electron deficient species, so the electron-donating effect of alkyl groups help to stabilize it. With more alkyl groups involved, the radical is more stable.
- **Homolytic bond dissociation energy** comparison: Homolytic cleavage of C-H bond produces carbon radical. The C-H bond in different structure has different bond dissociation energy. Let's compare two different types below, primary vs secondary:



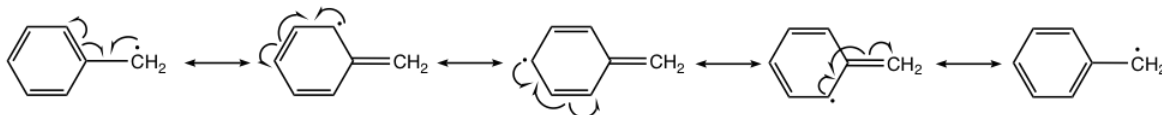
Since both radicals come from the same compound, propane, so the higher the homolytic bond dissociation energy means the higher the energy level of the resulting carbon radical. The bond energy of the 1° C-H is 10 kJ/mol higher in energy than the bond energy of the 2° C-H, therefore the secondary radical is more stable than the primary one.

Other than the above reasons, there is another effect that affect the stability of radicals. For example, the following radical exhibits special stability, that is even more stable than other regular tertiary radical, although it is a primary radical. Why? This is because of another effect — **resonance effect**!



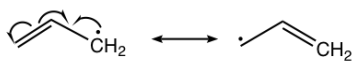
benzylic radical

The radical here is not a regular primary radical, it is on the position that is beside the benzene ring. The position right next to the benzene ring is call the **benzylic** position, and this radical is a **benzylic radical**. Because of the presence of benzene ring, the benzylic radical has total five resonance contributors. According to resonance effect, the more resonance contributors available, the better the electron density dispersed, the more stable the species is.



resonance effect: benzylic radical is stabilized by resonance structures

The resonance effect also helps to stabilize the **allylic radical** as well. The carbon that is right next to the C=C double bond is the **allylic** position. The resonance structures of an allylic radical example are shown below. Both benzylic and allylic radicals are more stable than the tertiary alkyl radicals because of resonance effects.



allylic radical is stabilized by resonance structures

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