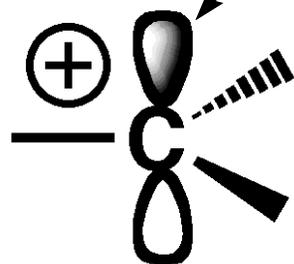


Carbocation Intermediates

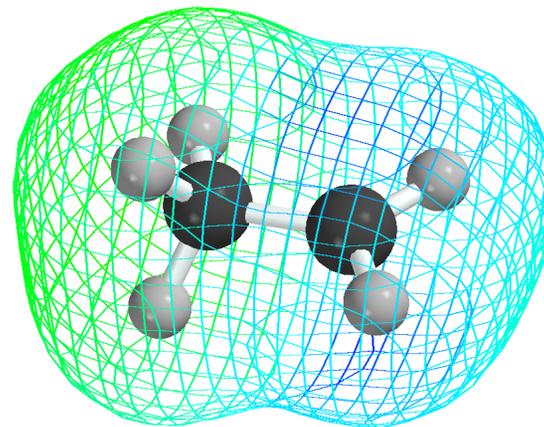
Carbocations are common intermediates in organic chemistry. We have encountered carbocations in $[S_N1]$ substitution and $[E1]$ elimination. Although carbocations are never present in very high concentrations (because they are unstable and highly reactive), they do open up a reaction pathway through which important chemistry ensues.

Carbocations have a carbon-centered empty p-orbital



carbocation

- 6-electron species
- trigonal planar geometry
- sp^2 hybridized
- empty p orbital on carbon

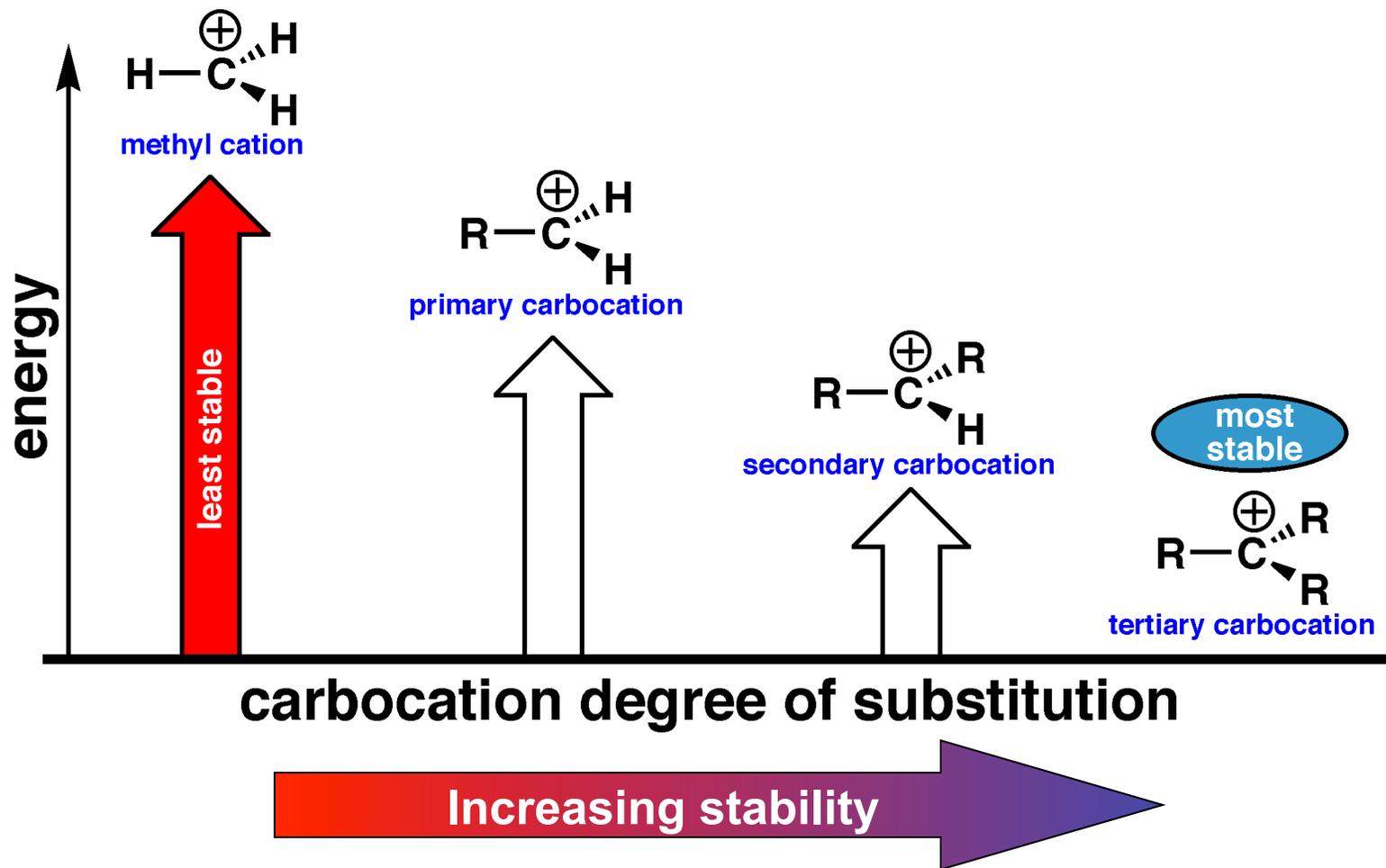


Electrostatic potential map for the ethyl carbocation. Regions colored **blue** are the most positive.



Stability of Carbocation Intermediates

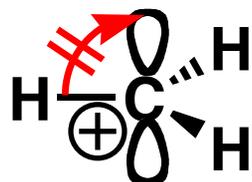
Certain carbocations are more easily formed than others. Only if the carbocation can be formed easily does it open a viable pathway. We thus need to understand how carbocation stability relates to structure, and how this structure relates to reactivity. A simple rule predicts stability for carbocations: *the more nonhydrogen substituents attached to a carbocation, the greater is its stability.*



π -type $\sigma \rightarrow a$ Resonance Interaction Stabilizes Carbocations

Why are substituted carbocations more stable than unsubstituted carbocations? The carbocation is a 6-electron species; any atom (or bond) that supplies this electron deficient carbon with electron density increases its stability. Electrons in bonds that are **directly attached** to the carbocation do not offer any help because the filled and empty orbitals are perpendicular and incapable of overlapping. However, electrons in **bonds that are one atom away** from the carbocation center are able to donate some of their electron density through a $\sigma \rightarrow a$ (π -type) interaction.

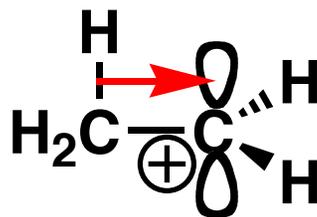
The $\sigma \rightarrow a$ filled \rightarrow empty orbital interaction of hyperconjugation



methyl cation

least stable carbocation

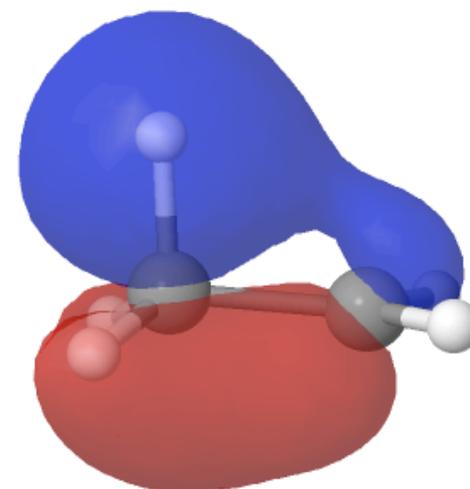
bonds directly attached to the carbocation do not share their electron density



ethyl cation

stabilized by hyperconjugation

bonds directly attached to a carbocation substituent do share their electron density



<http://www.chemtube3d.com/index.html>

Nucleophilic substitution	Simple S_N2 reaction
Elimination	S_N1 and S_N2
Electrophilic aromatic substitution	Carbocation structure and stability