# 16.2: ALLYLIC CATIONS

RESONANCE AND ALLYLIC CARBOCATION STABILITY

Conjugation occurs when p orbital on three or more adjacent atoms can overlap. Conjugation tends to stabilize molecules. Allylic carbocations are a common conjugated system. The resonance structures below help explain the stability of allylic carbocations. The true structure of the conjugated allyl carbocation is a hybrid of of the two resonance structure so the positive charge is delocalized over the two terminal carbons. This delocalization stablizes the allyl carbocation making it more stable than a normal primary carbocation.
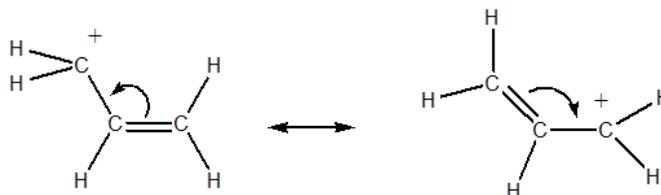
The positive charge of a carbocation is contained in a p orbital of a sp^2 hybridized carbon. This allows for overlap with double bonds. The positive charge is more stable because it is spread over 2 carbons.
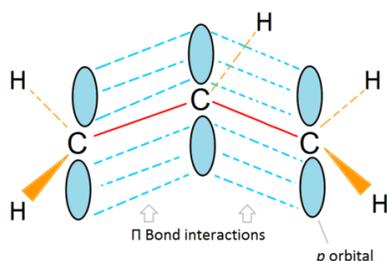
MOLECULAR ORBITALS AND ALLYLIC CARBOCATION STABILITY

The stability of the carbocation of propene is due to a conjugated π electron system. A "double bond" doesn't really exist. Instead, it is a group of 3 adjacent, overlapping, non-hybridized p orbitals we call a **conjugated π electron system**. You can clearly see the interactions between all three of the p orbitals from the three carbons resulting in a really stable cation. It all comes down to where the location of the electron-deficient carbon is.

Molecular orbital descriptions can explain allylic stability in yet another way using 2-propenyl. Fig.6
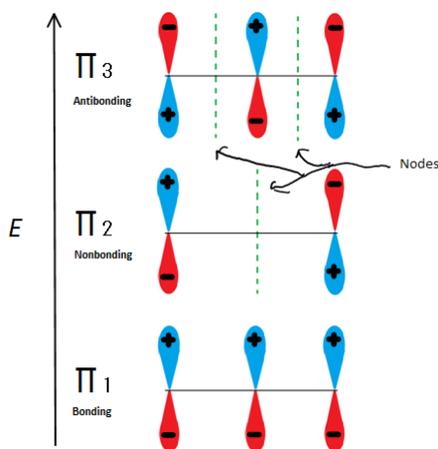
Figure: The 3 possible Molecular orbitals of 2-propenyl

If we just take the π molecular orbital and not any of the s, we get three of them. π_1 is bonding with no nodes, π_2 is nonbonding (In other words, the same energy as a regular p-orbital) with a node, and π_3 is antibonding with 2 nodes (none of the orbitals are interacting). The first

two electrons will go into the π_1 molecular orbital, regardless of whether it is a cation, radical, or anion. If it is a radical or anion, the next electron goes into the π_2 molecular orbital. The last anion electron goes into the nonbonding orbital also. So no matter what kind of carbon center exists, no electron will ever go into the antibonding orbital.

The Bonding orbitals are the lowest energy orbitals and are favorable, which is why they are filled first. Even though the nonbonding orbitals can be filled, the overall energy of the system is still lower and more stable due to the filled bonding molecular orbitals.

This figure also shows that π_2 is the only molecular orbital where the electrion differs, and it is also where a single node passes through the middle. Because of this, the charges of the molecule are mainly on the two terminal carbons and not the middle carbon.

This molecular orbital description can also illustrate the stability of allylic carbon centers in figure 7.
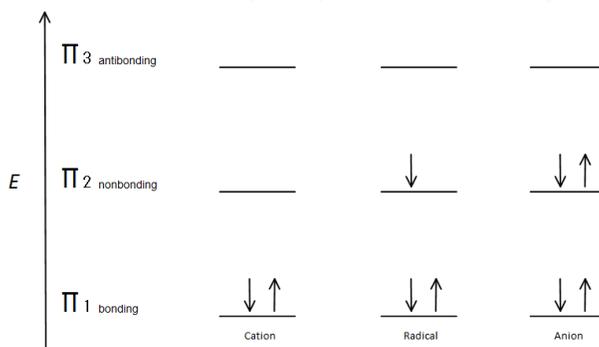
Figure: Diagram showing how the electrons fill based on the Aufbau principle.

The π bonding orbital is lower in energy than the nonbonding p orbital. Since every carbon center shown has two electrons in the lower energy, bonding π orbitals, the energy of each system is lowered overall (and thus more stable), regardless of cation, radical, or anion.

RELATIVE STABILITIES OF CARBOCATIONS
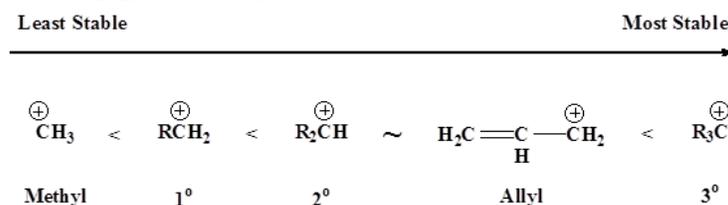
ALLYLIC RADICALS

As organic chemists, we are particularly interested in radical intermediates in which the unpaired electron resides on a carbon atom. Experimental evidence indicates that the three bonds in a carbon radical have trigonal planar geometry, and therefore the carbon is considered to be sp^2-hybridized with the unpaired electron occupying the perpendicular, unhybridized 2p$_z$orbital. Contrast this picture with carbocation and carbanion intermediates, which are both also trigonal planar but whose 2p$_z$ orbitals contain zero or two electrons, respectively.
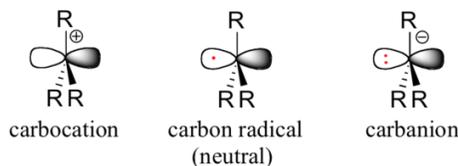
The trend in the stability of carbon radicals parallels that of carbocations (section 8.4B): tertiary radicals, for example, are more stable than secondary radicals, followed by primary and methyl radicals. This should make intuitive sense, because radicals, like carbocations, can be considered to be electron deficient, and thus are stabilized by the electron-donating effects of nearby alkyl groups. Benzylic and allylic radicals are more stable than alkyl radicals due to resonance effects - an unpaired electron can be delocalized over a system of conjugated pi bonds. An allylic radical, for example, can be pictured as a system of three parallel 2p$_z$ orbitals sharing three electrons.

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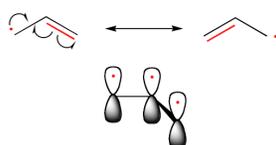
This can also explain why allylic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

> ### Exercise
>
> **2.** Draw the bond-line structure for the most stable carbocation that can be formed from each hydrocarbon below. Arrange the carbocations in order of decreasing stability.
>
>
>
> **Answer**
>
> **2.** Carbocations in order of decreasing stability.
>
>
>
> tertiary allylic   secondary benzylic   primary allylic
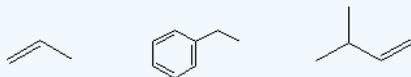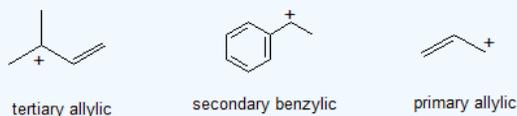
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