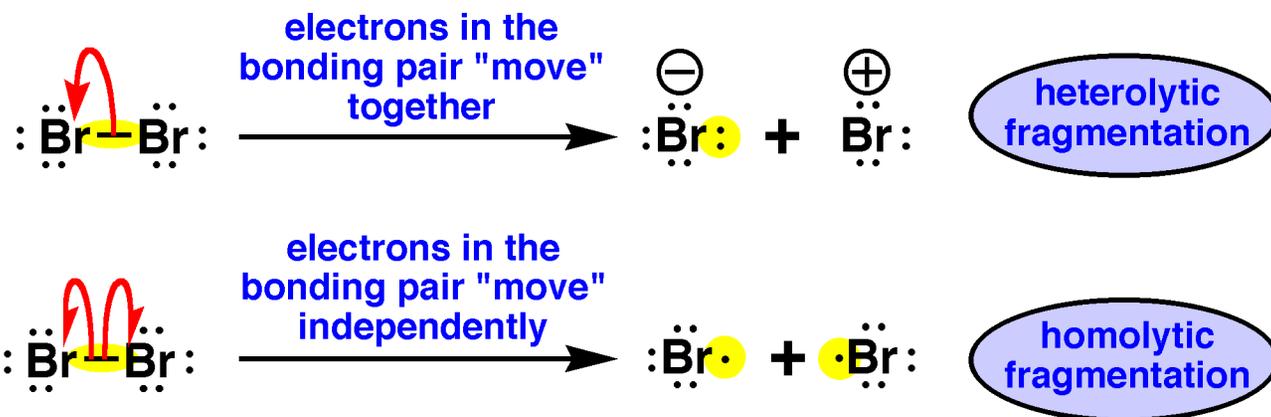


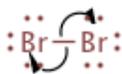
Homolytic vs. Heterolytic Fragmentation

Most organic transformations involve the movement of electron pairs (heterolytic reactions). There are a few important addition reactions, however, in which the electron reconfiguration involves the movement of single electrons. Whereas heterolytic bond cleavage leads to ion pairs, homolytic bond cleavage results in unpaired electrons – or free radicals. Some weak bonds have a tendency to fragment homolytically (e.g., peroxides, halogens). Chemists use a slight variation of curved arrow notation to show the movement of single electrons. For single electron movement, “fishhook” arrows, i.e., single headed arrows are drawn. The difference in these two notations is illustrated below for heterolytic vs. homolytic fragmentation of Br₂.



The “fishhook”
arrow tool.

How it looks
in ACE...



ACE mechanism calculator

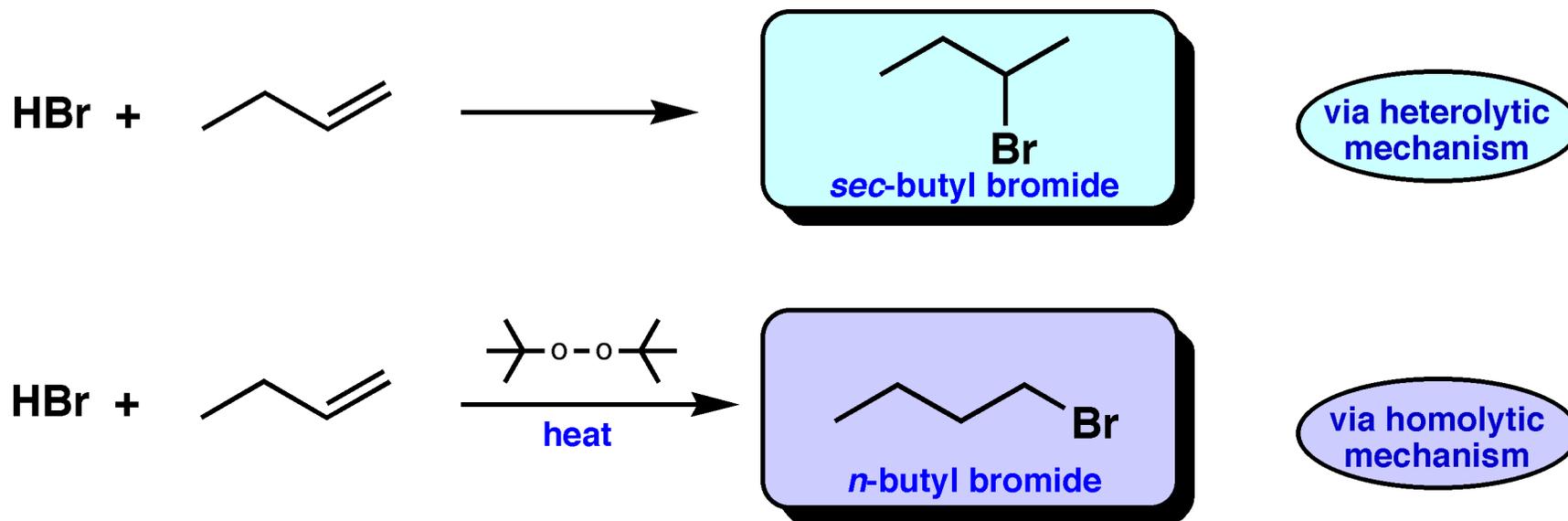


<http://aceorganic.pearsoncmg.com/epoch-plugin/public/mechmarvin.jsp>



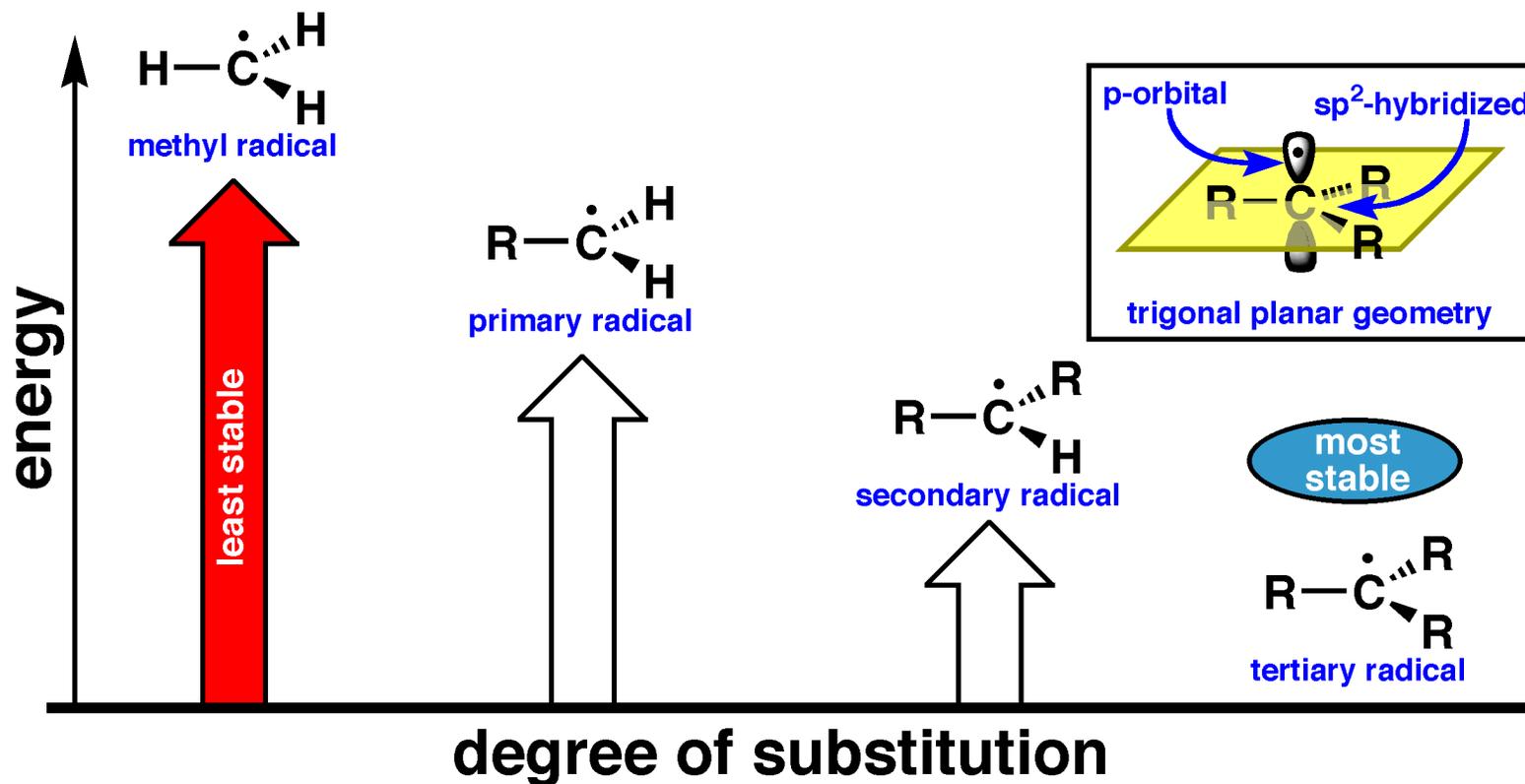
Comparing Homolytic and Heterolytic Addition

When peroxides are heated, they fragment homolytically. This behavior can be used to initiate addition reactions that proceed via radical intermediates. A consequence of the different reaction mechanism is that the regiochemistry of addition varies from that seen for the heterolytic case, as the comparisons below illustrate.



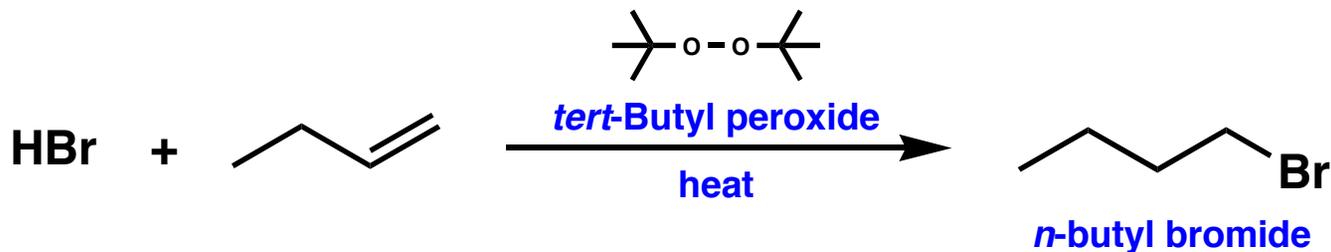
Stability of Carbon-Centered Radicals

In order to rationalize the reactivity trends seen above, we must first understand how radical stability depends on structure. The radical is a half-occupied electron pair domain (“open shell”). The geometry at carbon is approximately planar, and the single electron can be assumed to occupy the p-orbital of an sp^2 -hybridized atom. Since the carbon atom has 7 electrons, one short of the desired octet, it is electron deficient, and stability as a function of substitution follows the same trend found for carbocations.



The Radical Chain Mechanism

A **chain mechanism** has repeating characteristics. Species produced at the end reenter the mechanism to cause it to start all over. Radical reactions are often of this type. Chain mechanisms have three events in common: **initiation** events, **propagation** events and **termination** events. For radical chain mechanisms, initiation events are what create the radicals. Propagation events are what produce products and these are the steps that repeat in what are known as cycles, (like the links of a chain, hence the name chain mechanism). A single radical from an initiation event may yield several cycles of propagation. Since each cycle produces product, a single radical can account for several equivalents of product. The termination events consume radicals and shut down the propagation cycles.

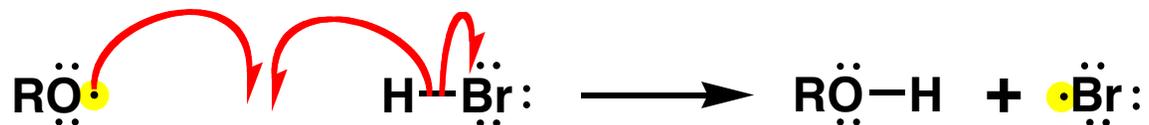


The thermally induced bond homolysis of peroxides is a common way to initiate radical reactions. The oxygen-oxygen bond of peroxides is a weak covalent bond of 47 kcal/mol and hence is readily susceptible to thermal dissociation. The result is a pair of oxygen-centered radicals.

Initiation

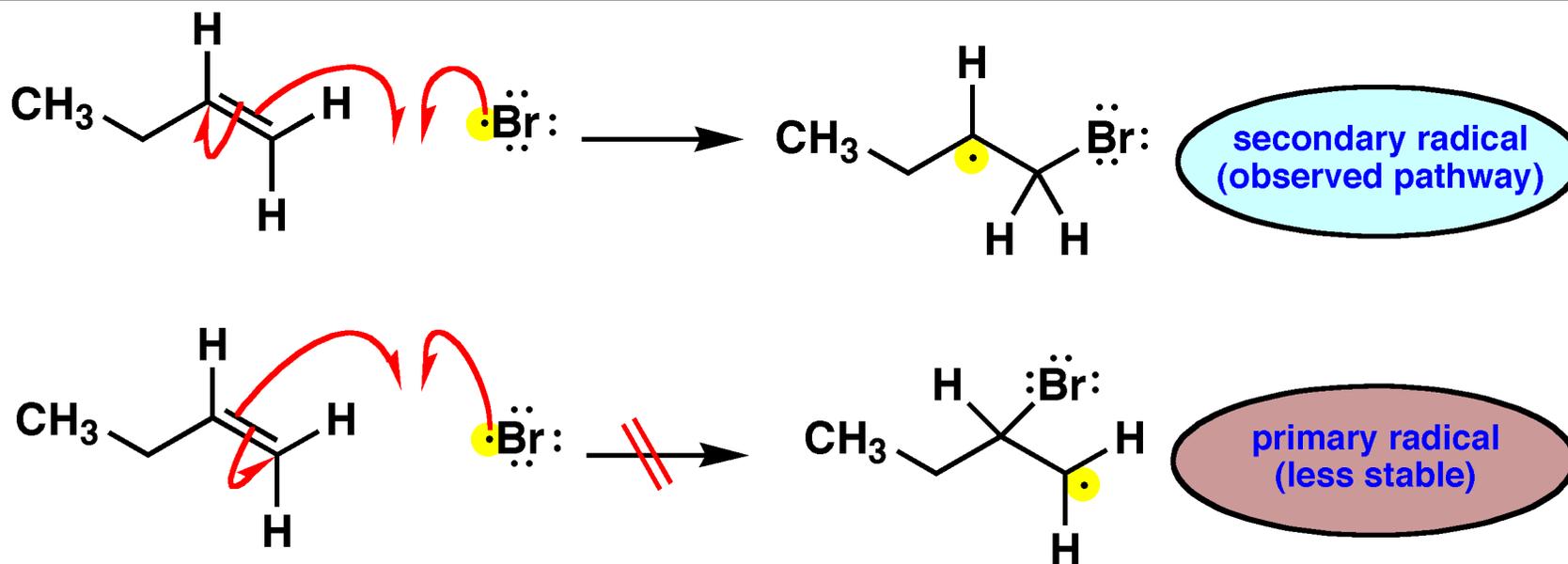


Thermal homolysis of peroxides results in a pair of oxygen-centered radicals. The next step in initiation involves HBr. A newly formed oxygen-centered radical abstracts a hydrogen atom from H-Br resulting in a bromine-centered radical and a hydroxyl group. The bromine-centered radical then enters the propagation cycle.

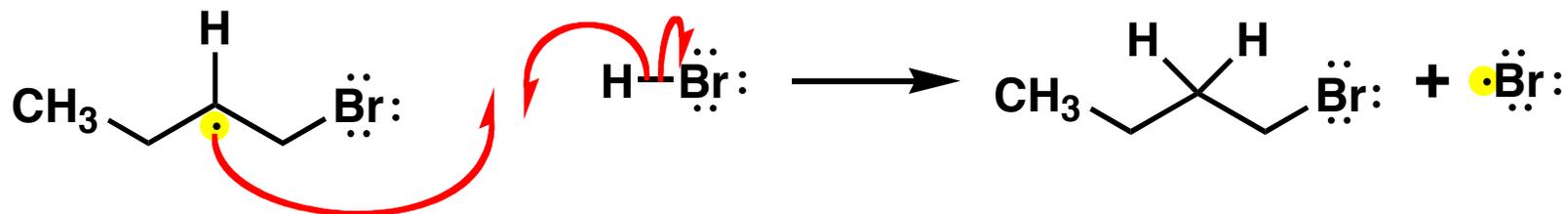


Propagation

The first step of the propagation cycle involves the addition of the bromine-centered radical to an alkene. This step creates a carbon-centered radical, and it determines the isomer that is formed (i.e., *n*-butyl vs. *sec*-butyl bromide). The formation of the most stable carbon-centered radical is what governs the outcome of this crucial step. By having the bromine-centered radical add to the terminal position of the alkene, a secondary carbon-centered radical results. This pathway is lower energy than the addition that leads to a primary radical.



The second half of propagation involves the carbon-centered radical abstracting a hydrogen atom from another molecule of HBr. This regenerates a bromine-centered radical along with the alkene addition product. The bromine-centered radical is ready to reenter a new chain propagation cycle.



Termination

Termination events are the ways that radicals annihilate themselves. All propagation steps involve a radical combining with a non-radical species. Through combination of a pair of radicals, the radicals will disappear. Because the concentration of radicals tends to be very low, these events are relatively rare. Some examples of termination reactions are shown below. All of them involve the combination of two radicals, and they produce non-radical products.

