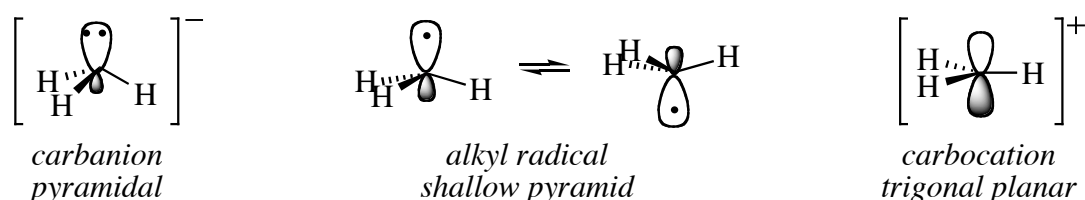


Chapter 15. Free Radical Reactions

A free radical is a species containing one or more unpaired electrons. Free radicals are electron-deficient species, but they are usually uncharged, so their chemistry is very different from the chemistry of even-electron electron-deficient species such as carbocations and carbenes.

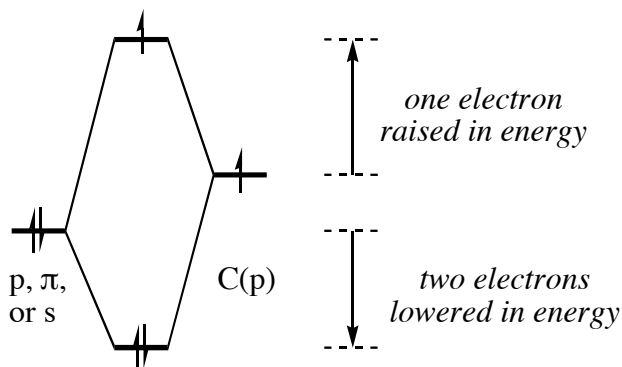
The alkyl radical ($\cdot\text{CR}_3$) is a seven-electron, electron-deficient species. The geometry of the alkyl radical is considered to be a shallow pyramid, somewhere between sp^2 and sp^3 hybridization, and the energy required to invert the pyramid is very small. In practice, one can usually think of alkyl radicals as if they were sp^2 -hybridized.



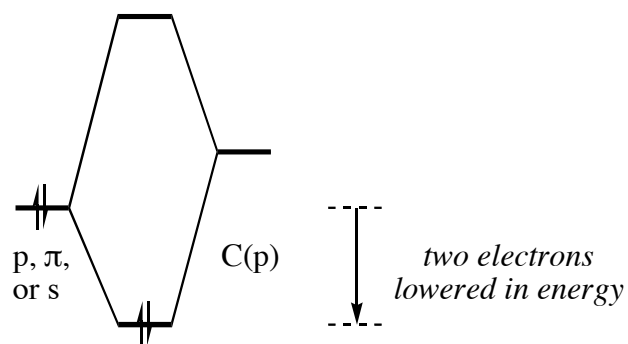
Both alkyl radicals and carbocations are electron-deficient species, and the structural features that stabilize carbocations also stabilize radicals. Alkyl radicals are stabilized by adjacent lone-pair-bearing heteroatoms and π bonds, just as carbocations are, and the order of stability of alkyl radicals is $3^\circ > 2^\circ > 1^\circ$. However, there are two major differences between the energy trends in carbocations and alkyl radicals.

- A C atom surrounded by seven electrons is not as electron-deficient as a C atom surrounded by six electrons, so alkyl radicals are generally not as high in energy as the corresponding carbocations. Thus, the very unstable aryl and 1° alkyl carbocations are almost never seen, whereas aryl and 1° alkyl radicals are reasonably common.
- The amount of extra stabilization that adjacent lone pairs, π bonds, and σ bonds provide to radicals is not as great as that which they provide to carbocations. The reason is that the interaction of a filled AO or MO with an empty AO (as in carbocations) puts two electrons in an MO of reduced energy, whereas the interaction of a filled AO or MO with a half-filled AO (free radicals) puts two electrons in an MO of reduced energy and one electron in an MO of increased energy.

Orbital interaction diagram for radicals



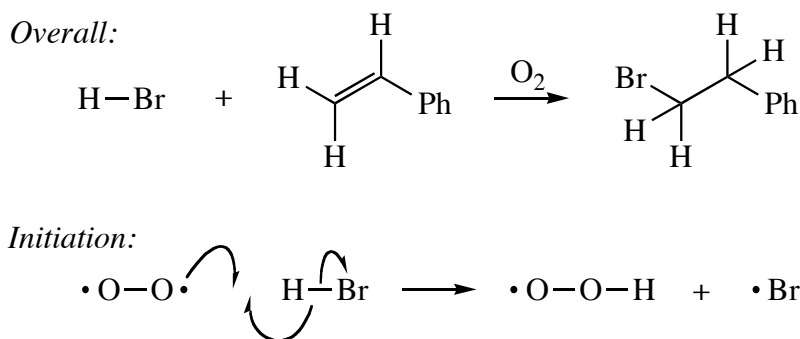
Orbital interaction diagram for carbocations



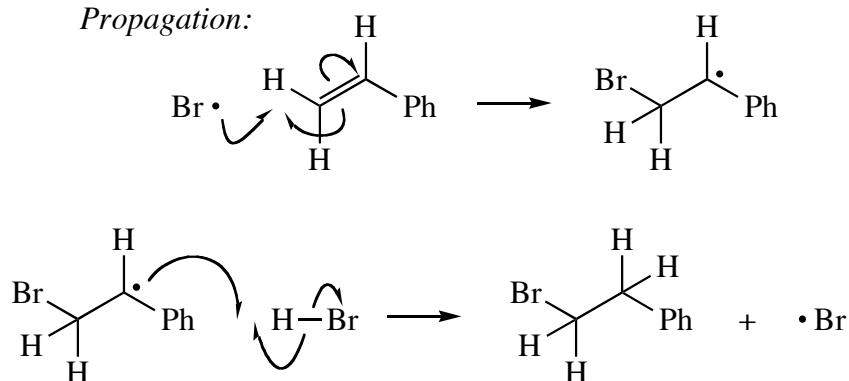
Even though adjacent lone pairs, π bonds, and σ bonds do not stabilize radicals as much as they stabilize carbocations, the cumulative stabilizing effect of several such groups on a radical can be considerable. Benzylic radicals (those with the radical on a C atom next to a benzene ring, but not in a benzene ring) are particularly low in energy, as the radical center is stabilized by resonance with three π bonds.

15.1 Addition of HBr to Alkenes.

The anti-Markovnikov addition of HBr to alkenes was probably the first free-radical addition reaction to be discovered. The discovery was inadvertent; around the turn of the twentieth century, scientists studying the regiochemistry of addition of HBr to alkenes found that the proportion of Markovnikov to anti-Markovnikov addition products varied inexplicably from run to run. Eventually it was discovered that impurities such as O_2 and peroxides greatly increased the amount of anti-Markovnikov addition product. The results were later explained by a free-radical addition mechanism. The anti-Markovnikov regiochemistry derives from the addition of $Br\cdot$ radical to the less substituted C atom of the alkene (steric reasons) to give the more stable, more substituted radical (electronic reasons). In a polar, electrophilic addition reaction, the regioselectivity would be such that Br would add to the more substituted C atom of the alkene.



Propagation:

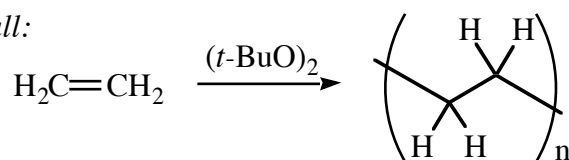


In contrast to HBr, the acids HCl and HI do not undergo free-radical addition to alkenes, even in the presence of peroxides or O_2 . Abstraction of $\text{H}\cdot$ from HCl is too endothermic, and addition of $\text{I}\cdot$ to an alkene is too endothermic.

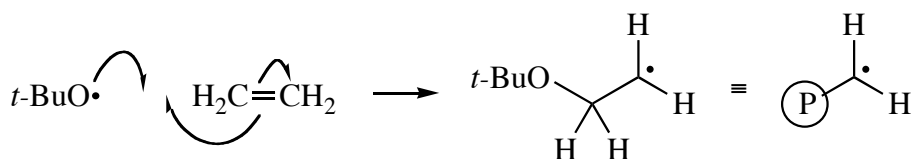
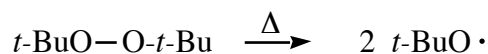
15.2 Free-Radical Polymerization of Alkenes.

The most important free-radical chain reaction conducted in industry is the free-radical polymerization of ethylene to give polyethylene. Industrial processes usually use $(t\text{-BuO})_2$ as the initiator. The $t\text{-BuO}\cdot$ radical adds to ethylene to give the beginning of a polymer chain. The propagation part has only one step: the addition of an alkyl radical at the end of a growing polymer to ethylene to give a new alkyl radical at the end of a longer polymer. The termination steps are the usual radical-radical combination and disproportionation reactions.

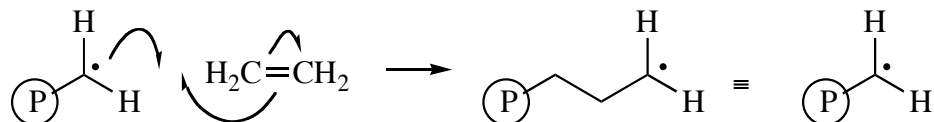
Overall:



Initiation:

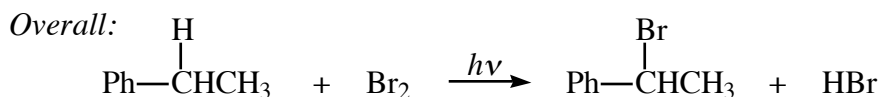


Propagation:

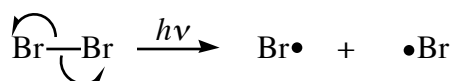


15.3 Free-Radical Substitution of Alkanes.

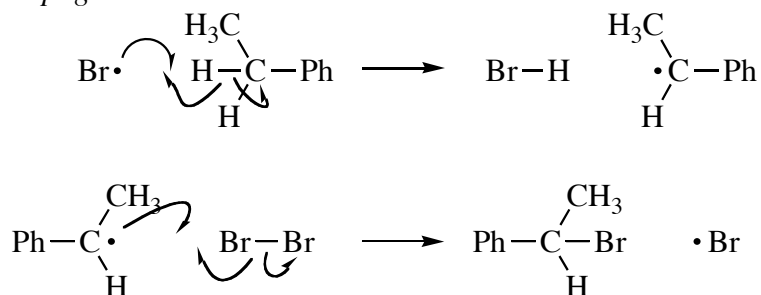
Probably the best-known example of a free-radical reaction is the halogenation of alkanes with Br_2 or NBS. This chain reaction is initiated by homolytic cleavage of Br_2 induced by light. The propagation part consists of two atom abstraction reactions.



Initiation:

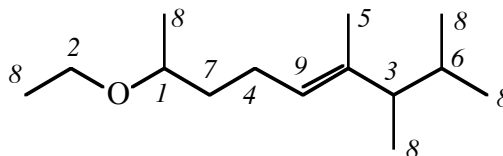


Propagation:

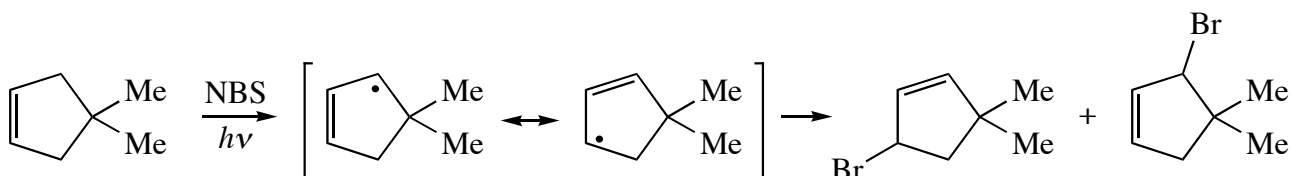


When more than one kind of H atom is present, the H atom that is removed is usually the one that will leave behind the lowest energy radical. H atoms are never removed from $\text{C}(\text{sp})$ or $\text{C}(\text{sp}^2)$, only from $\text{C}(\text{sp}^3)$. Among $\text{C}(\text{sp}^3)\text{-H}$ bonds, it is easiest to remove a H if a heteroatom such as N or O is attached to the C. If no such H atom is present, then the H atom that is removed is best *allylic* or *benzylic* (the C is attached to a $\text{C}=\text{C}$ π bond or to a benzene ring). If there are no allylic or benzylic H atoms, then the order of reactivity of H atoms is $3^\circ > 2^\circ > 1^\circ$.

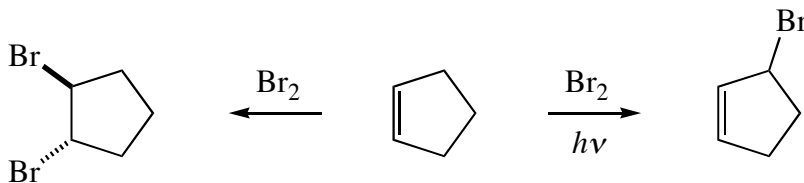
Ease of removal of H (1 easiest, 9 hardest)



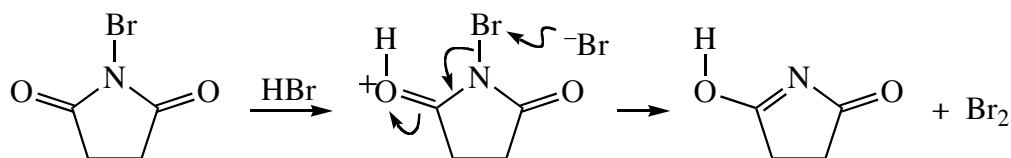
Free-radical halogenation is most commonly applied to allylic or benzylic halogenation, as the radicals formed at these positions are most stable. Of course, in allylic halogenation, transposition of the double bond can easily occur.



Note that alkenes can react with Br_2 by either an electrophilic addition reaction, to give 1,2-dibromoalkanes, or by a free-radical substitution reaction, giving 3-bromoalkenes. The former pathway predominates in the dark, whereas the latter pathway predominates in the presence of strong light.



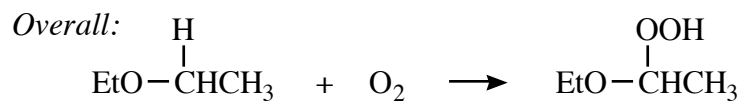
NBS (N-bromosuccinimide) is often used as the Br source in free-radical brominations. In these reactions, it is thought that Br_2 is the actual halogenating agent. The Br_2 is generated by reaction of HBr (the by-product of halogenation) with NBS. This polar reaction intervenes between the $\text{H}\cdot$ abstraction and $\text{Br}\cdot$ abstraction steps of the propagation part of the chain mechanism.



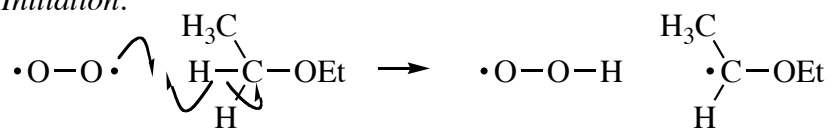
Elemental chlorine can be used in free-radical halogenation reactions, too, but these reactions are less easily controlled, because the $\text{Cl}\cdot$ radical is more reactive than the $\text{Br}\cdot$ radical and hence less selective. The reagents $t\text{-BuOCl}$ and SO_2Cl_2 are used as alternative chlorinating agents. The $\text{F}\cdot$ radical is so reactive, and the reaction $\text{F}\cdot + \text{C-H} \rightarrow \text{H-F} + \text{C}\cdot$ is so exothermic, that free-radical fluorinations result in violent and uncontrollable exotherms (explosions). At the other extreme, free-radical iodinations of alkanes do not work well at all, as the $\text{H}\cdot$ abstraction step is too endothermic.

15.4 Autoxidation.

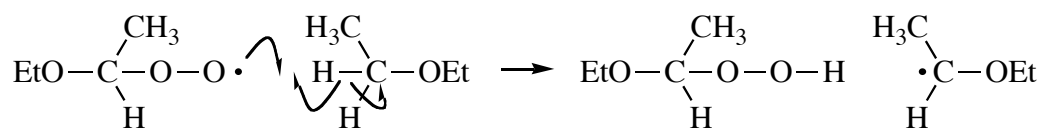
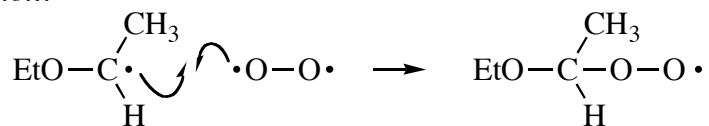
The substitution of H with OOH in organic compounds is called *autoxidation*. (“Autoxidation” is a misnomer, because the substrate is not oxidizing itself; O_2 is doing the oxidizing.) Autoxidation proceeds by a free-radical chain mechanism. Note that the mechanism for oxidation includes a very rare radical–radical combination step in the propagation part. The radical–radical combination step doesn’t terminate the chain in this particular reaction because O_2 is a 1,2-diradical. Ethers are particularly prone to autoxidation because O can stabilize a radical at the adjacent C atom.



Initiation:



Propagation:



Autoxidation is the reaction that leads to fires in oily rags that have been left in the garage. It is also a reaction that occurs as part of the aging process.