

BOND FISSION - I

A covalent bond is formed when electrons are shared between two atoms in the classical sense. A single bond (sigma bond) is thus made up of two electrons. Now a chemical reaction takes place when old bonds are broken and new ones are created. So how can one break a single bond—there are plainly two ways to go about breaking a bond as shown below.

Homolytic fission

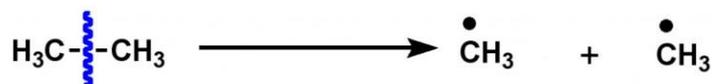


Figure 1. Homolysis

Homolytic fission is where each atom of the bond keeps an electron each resulting in species called free radicals. Radicals are important intermediates in organic chemistry and we will talk about them later. As the bond breaks to give two similar species each keeping an electron this form of bond breaking is called *Homolytic Fission*.

Heterolytic fission

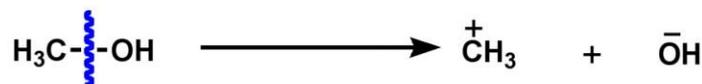


Figure 2. Heterolysis

In this case we can see that one of the atoms carry a negative charge after bond cleavage indicating that it has both the electrons of the bond and the other has no electrons at all. Hence it is electron deficient thus positively charged. As the electrons are not divided equally after bond cleavage this is called *Heterolytic Fission*. In a case the C atom carries a positive charge it is called a carbocation and in the case it carries both the electrons of the broken bond and is negatively charged, it is quite intuitively called a Carbanion. Carbocation and Carbanions are the most important carbon intermediates in organic chemistry and hence warrant further discussion.

Please note that both types of fissions are applicable to both homoatomic and heteroatomic bonds (bonds between two different atoms say C-N or C-O). Now let us discuss the three intermediates we talked about in some detail.

Free radicals

These are neutral intermediates, formed due to homolytic cleavage of a single bond. Some common bonds which cleave to give free radicals in organic chemistry are shown: C-O, C-Cl, C-Br, C-I, C-C, C-H. Carbon free radicals are mainly generated by:

- i. Photolysis (action of light) like acetone alpha cleavage
- ii. Other radical initiator like allylic bromination by N-Bromosuccinimide (NBS)

There has been a certain degree of debate as to what the shape and geometry of a free radical is like. Revisiting the theory of hybridization, there can be two basic shapes of these radicals.

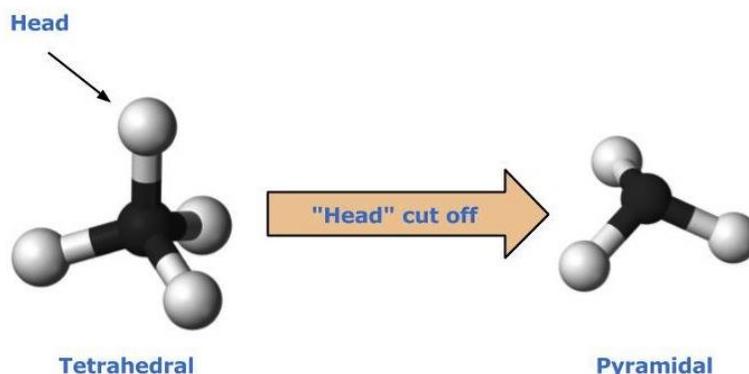


Figure 3. An illustration to describe pyramidal shape

If the centre carbon atom of the radical is sp^3 hybridized (remember the one which was made of one s and three orbitals as in CH_4), the geometry will be tetrahedral.¹ But in the case of a radical there are only three groups attached to the sp^3 hybridized carbon atom so they we will have a shape of what resembles a pyramid—it's a tetrahedron with its head cut off. So sp^3 hybridized radicals are pyramidal in shape. The single electron of the radical would then be housed in a sp^3 orbital. The other option is sp^2 hybridization. In that case the C atom is sp^2 hybridized, so as discussed previously the shape would be planar with the single electron in the unhybridized p-orbital with the three substituents having sp^2 hybridized bonds.

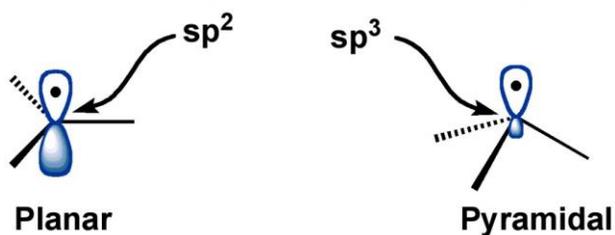


Figure 4. Two different geometries of free radicals. The single electrons are shown as black dots.

So to summarize free radicals:

- Formed under activation by light or use of additional compounds called Radical Initiators.
- They are very reactive, because they have an unpaired electron which wants to get paired up.
- They are either pyramidal or planar with the lone electron in their sp^3 or p orbitals respectively.

- Because of their high reactivity, they tend to be less selective. In simple terms it means that it sometimes difficult to predict what products are formed in reactions which involve free radicals and we actually get several products from a single reaction.

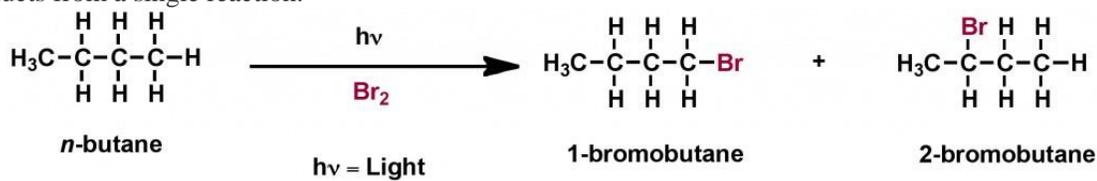


Figure 5. Bromination of alkane

This reaction shows the formation of two products with the Br atom attached to different carbons.

Source : <http://padakshep.org/otp/subjects/chemistry/organic-chemistry/bond-fission/>