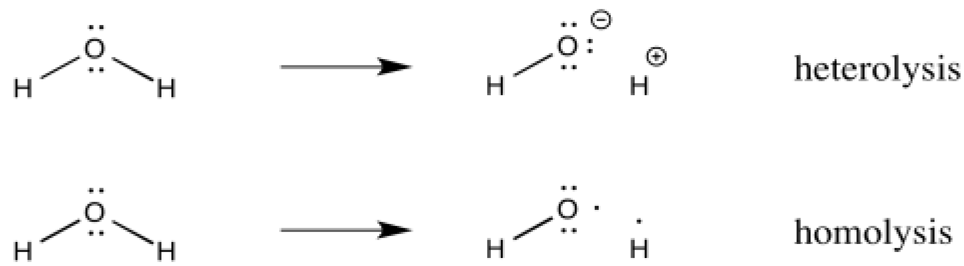
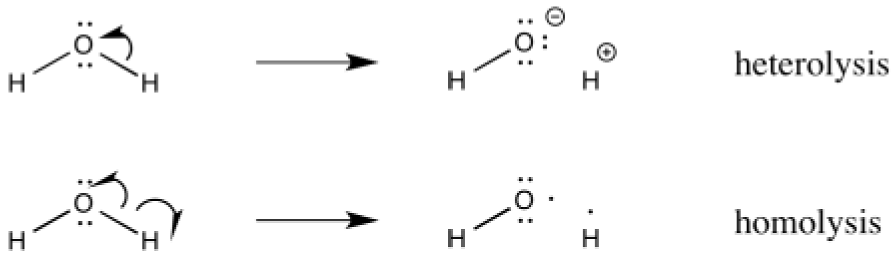
RADICAL INITIATION: BOND HOMOLYSIS

Sometimes, radicals form because a covalent bond simply splits in half. Two atoms that used to be bonded to each other go their separate ways. Each atom takes with it one electron from the former bond. This process is called homolysis, meaning the bond is breaking evenly. In contrast, heterolysis is the term for a bond that breaks via ionization, with one atom getting both electrons from the bond.



- Homolysis describes breaking a bond in half, with one electron going to each side of the former bond.

In pictures, we show this process using curved arrows, but the arrows we use are slightly different from the ones you may be used to seeing in polar reaction chemistry. Instead of a regular arrowhead, we use a half arrowhead. This kind of arrow looks a little more like a fish hook. It is easy to remember the roles of the two kinds of arrows, because a full arrowhead describes the movement of an electron pair, whereas a half arrowhead describes the movement of only one electron.



Why would a covalent bond simply break apart? There are really a number of factors and a number of events that may result in this situation. The simple part of the story is that the bond must have been weak in the first place. There was enough energy available in the form of heat transferred from the surroundings (or sometimes in the form of light) to overcome the stabilization energy of the bond.

What makes a bond weak or strong? That is a complicated question. Many factors influence bond strength. However, two of the main factors responsible for covalent bond strength are the degree of electron sharing because of "overlap" and the degree of bond polarity resulting from "exchange". Most strong covalent bonds rely on a mixture of these two factors.

One fairly common feature in homolysis is a bond between two atoms of the same kind. For example, elemental halogens often undergo homolysis pretty easily. The ease with which these bonds can be split in half is illustrated by their low bond dissociation energies. Not much energy needs to be added in order to overcome the bonds between these atoms.

Bond	Bond Dissociation Energy (kcal/mol)
H-H	105

C-C	85
N-N	65
O-O	47
F-F	37
S-S	45
Cl-Cl	57
Br-Br	45
Sn-Sn	45
I-I	35

This propensity for radical formation can be understood in terms of the lack of a polar component in these bonds. These atoms rely solely on atomic overlap to share electrons with each other.

There is a notable exception to the rule that homoatomic bonds are inherently weak, and that is a carbon-carbon bond. Its bond dissociation energy is listed in the table for comparison with the halogens. The relative strength of carbon-carbon bonds gives rise to a multitude of carbon-based "organic" compounds in nature. The formation of bonds between like atoms is called "catenation"; carbon is the world champion.

Source: http://employees.csbsju.edu/cschaller/Reactivity/radical/radicals%20homolysis.htm