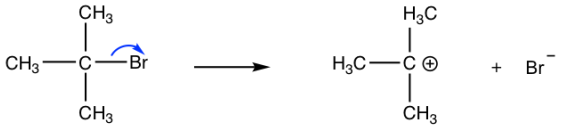
9.1: Homolytic and Heterolytic Cleavage

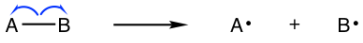
For the reactions we learned so far, bond breaking occurs in the way that one part of the bond takes **both** electrons (the electron pair) of the bond away. For example of S_N1 reaction, the leaving group Br leaves with the electron pair to form Br^- and carbocation intermediate.



example of heterolytic bond cleavage

This process is called **heterolytic bond cleavage**, the σ bond breaks heterolytically. As we have always been doing, an arrow with the **double-barbs** is used to show heterolytic cleavage, that is the transfer of electron pair specifically:

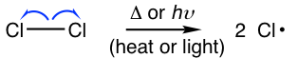
There is another type of bond breaking process, in which each part of the σ bond takes one electron away, as shown below:

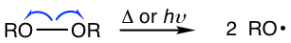


homolytic bond cleavage

This is called **homolytic cleavage** , or **homolysis** . The electron pair separate evenly to each part, and as a result both products contain a single electron. The species that contain one or more single electron is called radical (or free radical). Radicals are produced from homolytic cleavage. The arrow with sing-barb (like the shape of a fishhook) is used to show homolytic cleavage, that is single electron transfer specifically:

Homolysis occurs mainly for non-polar bonds, heat or light (delta is the symbol for heat; hv is used to show light) is needed to provide enough energy for initiating the process. For example:





Radical is another highly reactive reaction intermediate, because of the lack of octet. The substitution reaction we will learn in this chapter involves the radical intermediate.