

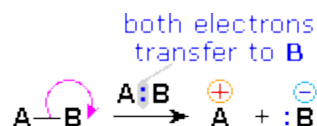
# Mechanisms of Organic Reactions

A detailed description of the changes in structure and bonding that take place in the course of a reaction, and the sequence of such events is called the **reaction mechanism**. A reaction mechanism should include a representation of plausible electron reorganization, as well as the identification of any intermediate species that may be formed as the reaction progresses. These features are elaborated in the following sections.

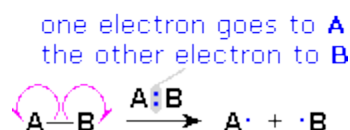
## 1. The Arrow Notation in Mechanisms

Since chemical reactions involve the breaking and making of bonds, a consideration of the movement of bonding ( and non-bonding ) valence shell electrons is essential to this understanding. It is now common practice to show the movement of electrons with curved arrows, and a sequence of equations depicting the consequences of such electron shifts is termed a **mechanism**. In general, two kinds of curved arrows are used in drawing mechanisms:

A full head on the arrow indicates the movement or shift of an electron pair:

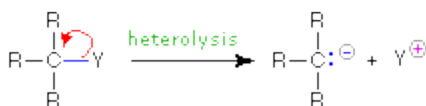
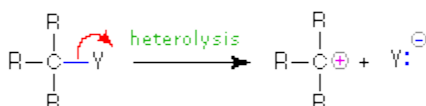
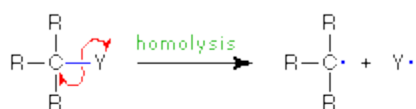


A partial head (fishhook) on the arrow indicates the shift of a single electron:

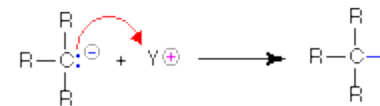
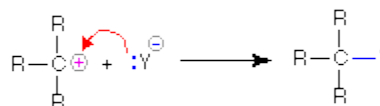
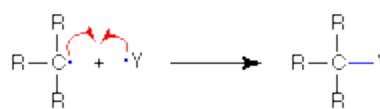


The use of these symbols in bond-breaking and bond-making reactions is illustrated below. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, as in the first example, this bond-breaking is called **homolysis**. If the bond breaks with both electrons of the shared pair remaining with one fragment, as in the second and third examples, this is called **heterolysis**.

### Bond-Breaking



### Bond-Making



## Other Arrow Symbols

Chemists also use arrow symbols for other purposes, and it is essential to use them correctly.

**The Reaction Arrow**



**The Equilibrium Arrow**



**The Resonance Arrow**



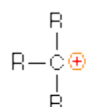
The following equations illustrate the proper use of these symbols:



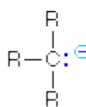
## 2. Reactive Intermediates

The products of bond breaking, shown above, are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as **reactive intermediates**, and are believed to be transient intermediates in many reactions. The general structures and names of four such intermediates are given below.

**Charged Intermediates**

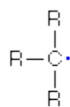


**A Carbocation**



**A Carbanion**

**Uncharged Intermediates**



**A Radical**



**A Carbene**

A pair of widely used terms, related to the Lewis acid-base notation, should also be introduced here.

**Electrophile:** An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.

**Nucleophile:** An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid).

Using these definitions, it is clear that carbocations ( called carbonium ions in the older literature ) are electrophiles and carbanions are nucleophiles. Carbenes have only a valence shell sextet of electrons and are therefore electron deficient. In this sense they are electrophiles, but the non-bonding electron pair also gives carbenes nucleophilic character. As a rule, the electrophilic character dominates carbene reactivity. Carbon radicals have only seven valence electrons, and may be considered electron deficient; however, they do not in general bond to nucleophilic electron pairs, so their chemistry exhibits unique differences from that of conventional electrophiles. Radical intermediates are often called **free radicals**. The importance of electrophile / nucleophile terminology comes from the fact that many organic reactions involve at some stage the bonding of a nucleophile to an electrophile, a process that generally leads to a stable intermediate or product. Reactions of this kind are sometimes called **ionic reactions**, since ionic reactants or products are often involved.

The shapes ideally assumed by these intermediates becomes important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compound like methane, CH<sub>4</sub>, has a tetrahedral configuration. Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration. Carbanions are pyramidal in shape ( tetrahedral if the electron pair is viewed as a substituent ), but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a p-orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Since three points determine a plane, the shape of carbenes must be planar; however, the valence electron distribution varies.

Source : <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/react1.htm#rx2>