



6.3: Bond Breaking and Bond Making

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:		$\text{A} \text{---} \text{B} \xrightarrow{\text{full head}} \text{A}^+ + \text{B}^-$ <p>both electrons transfer to B</p>
A partial head (fishhook) on the arrow indicates the shift of a single electron:		$\text{A} \text{---} \text{B} \xrightarrow{\text{partial head}} \text{A}^\cdot + \text{B}^\cdot$ <p>one electron goes to A the other electron to B</p>

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**.

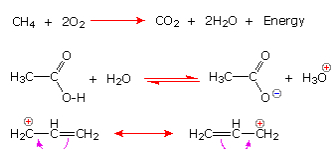
Bond-Breaking	Bond-Making
$\text{R}-\text{C}-\text{Y} \xrightarrow{\text{homolysis}} \text{R}-\text{C}^\cdot + \text{Y}^\cdot$ $\text{R}-\text{C}-\text{Y} \xrightarrow{\text{heterolysis}} \text{R}-\text{C}^+ + \text{Y}^-$ $\text{R}-\text{C}-\text{Y} \xrightarrow{\text{heterolysis}} \text{R}-\text{C}^- + \text{Y}^+$	$\text{R}-\text{C}^\cdot + \text{Y}^\cdot \longrightarrow \text{R}-\text{C}-\text{Y}$ $\text{R}-\text{C}^+ + \text{Y}^- \longrightarrow \text{R}-\text{C}-\text{Y}$ $\text{R}-\text{C}^- + \text{Y}^+ \longrightarrow \text{R}-\text{C}-\text{Y}$

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
\longrightarrow	\rightleftharpoons	\longleftrightarrow

The following equations illustrate the proper use of these symbols:



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	Uncharged Intermediates
$\text{R}-\text{C}^+$ <p>A Carbocation</p>	$\text{R}-\text{C}^\cdot$ <p>A Radical</p>
$\text{R}-\text{C}^-$ <p>A Carbanion</p>	$\text{R}-\text{C}:$ <p>A Carbene</p>

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. Some common examples of ionic reactions and their mechanisms may be examined by [Clicking Here](#)

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_4 , 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.

Contributors

- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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