13.1: Introduction

In chemistry, a **radical** (more precisely, a **free radical**) is an atom, molecule, or ion that has unpaired valence electrons or an open electron shell, and therefore may be seen as having one or more "dangling" covalent bonds.

With some exceptions, these "dangling" bonds make free radicals highly chemically reactive towards other substances, or even towards themselves: their molecules will often spontaneously dimerize or polymerize if they come in contact with each other. Most radicals are reasonably stable only at very low concentrations in inert media or in a vacuum.

Free radicals may be created in a number of ways, including synthesis with very dilute or rarefied reagents, reactions at very low temperatures, or breakup of larger molecules. The latter can be affected by any process that puts enough energy into the parent molecule, such as ionizing radiation, heat, electrical discharges, electrolysis, and chemical reactions. Indeed, radicals are intermediate stages in many chemical reactions.

History

The first organic free radical identified was triphenylmethyl radical. This species was discovered by Moses Gomberg in 1900 at the University of Michigan USA. Historically, the term *radical* in radical theory was also used for bound parts of the molecule, especially when they remain unchanged in reactions. These are now called functional groups. For example, methyl alcohol was described as consisting of a methyl "radical" and a hydroxyl "radical". Neither are radicals in the modern chemical sense, as they are permanently bound to each other, and have no unpaired, reactive electrons; however, they can be observed as radicals in mass spectrometry when broken apart by irradiation with energetic electrons.

Depiction in chemical reactions

In this chapter, we will learn about some reactions in which the key steps involve the movement of *single* electrons. You may recall from way back in section 6.1A that single electron movement is depicted by a single-barbed **'fish-hook'** arrow (as opposed to the familiar double-barbed arrows that we have been using throughout the book to show two-electron movement).

curved, two-barbed arrow:
two electron movement

curved, single-barbed ('fish-hook') arrow:
single electron movement
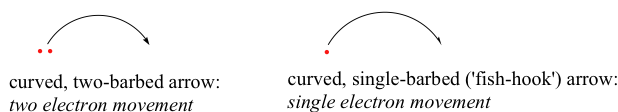
Single-electron mechanisms involve the formation and subsequent reaction of free radical species, highly unstable intermediates that contain an unpaired electron. We will learn in this chapter how free radicals are often formed from **homolytic cleavage**, an event where the two electrons in a breaking covalent bond move in opposite directions.

$$\text{X}\frown\text{X} \longrightarrow 2\ \text{X} \cdot$$

(In contrast, essentially all of the reactions we have studied up to now involve bond-breaking events in which both electrons move in the same direction: this is called **heterolytic cleavage**).

We will also learn that many single-electron mechanisms take the form of a radical chain reaction, in which one radical causes the formation of a second radical, which in turn causes the formation of a third radical, and so on.

$$\text{X}\cdot \ \ \text{H}\frown\text{Y} \longrightarrow \text{X}-\text{H} + \text{Y}\cdot \ \ \text{H}\frown\text{Z} \longrightarrow \text{Y}-\text{H} + \text{Z}\cdot$$

The high reactivity of free radical species and their ability to initiate chain reactions is often beneficial - we will learn in this chapter about radical polymerization reactions that form useful materials such as plexiglass and polyproylene fabric. We will also learn about radical reactions that are harmful, such as the degradation of atmospheric ozone by freon, and the oxidative damage done to lipids and DNA in our bodies by free radicals species. Finally, we will see how some enzymes use bound metals to catalyze high e

The geometry and relative stability of carbon radicals

As organic chemists, we are particularly interested in radical intermediates in which the unpaired electron resides on a carbon atom. Experimental evidence indicates that the three bonds in a carbon radical have trigonal planar geometry, and therefore the carbon is considered to be sp^2-hybridized with the unpaired electron occupying the perpendicular, unhybridized $2p_z$ orbital. Contrast this

picture with carbocation and carbanion intermediates, which are both also trigonal planar but whose $2p_z$ orbitals contain zero or two electrons, respectively.


carbocation   carbon radical   carbanion
                  (neutral)
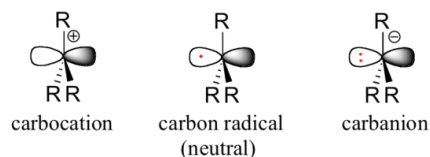
The trend in the stability of carbon radicals parallels that of carbocations (section 8.4B): tertiary radicals, for example, are more stable than secondary radicals, followed by primary and methyl radicals. This should make intuitive sense, because radicals, like carbocations, can be considered to be electron deficient, and thus are stabilized by the electron-donating effects of nearby alkyl groups. Benzylic and allylic radicals are more stable than alkyl radicals due to resonance effects - an unpaired electron can be delocalized over a system of conjugated pi bonds. An allylic radical, for example, can be pictured as a system of three parallel $2p_z$ orbitals sharing three electrons.
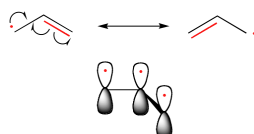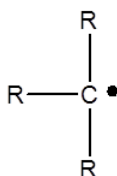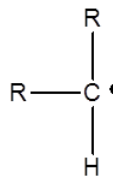

Trends in radical stability
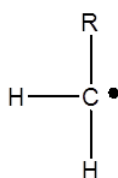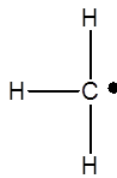
Primary   Methyl


Tertiary   Secondary

Allyic & Benzlic > 3º > 2º > 1º > Methyl

Template:ExampleStart
Exercise 17.1: Draw the structure of a benzylic radical compound, and then draw a resonance form showing how the radical is stabilized.
Template:ExampleEnd
With enough resonance stabilization, radicals can be made that are quite unreactive. One example of an inert organic radical structure is shown below.
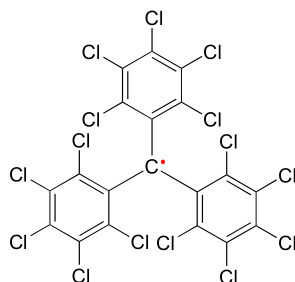
In this molecule, the already extensive resonance stabilization is further enhanced by the ability of the chlorine atoms to shield the radical center from external reagents. The radical is, in some sense, inside a protective 'cage'.

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