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5.111 Principles of Chemical Science
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Exceptions to Lewis Structure Rules: Free Radicals

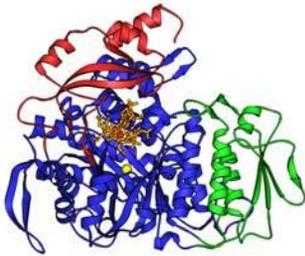
See lecture 10 (starting on page 3 of the notes) and lecture 11 for Lewis structures.

See lecture 12 for exceptions to Lewis structure rules.

Free radicals (or radicals) are molecules that have one or more unpaired electron. Due to the unpaired electron(s), most radicals are unstable and highly reactive.

Example 1) from page 1 of Lecture 12 notes: Free radicals in biology

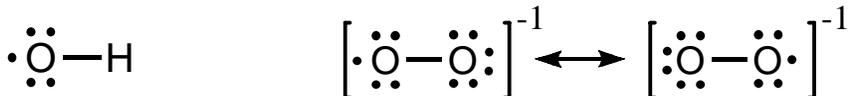
Free radicals in biology: a paradox

<p>Free radical species damage DNA.</p> <ul style="list-style-type: none"> Highly reactive oxygen radicals are a byproduct of metabolism and cause DNA damage (see information below*). Cigarette smoke contains free radicals that can damage DNA in lung cells and lead to cancer.  <ul style="list-style-type: none"> Antioxidants (such as vitamin A, C, and E) reduce DNA damage in the body by “trapping” radicals.  <p><i>blueberries are one of the most anti-oxidant rich foods</i></p>	<p>Free radicals are essential for life.</p> <ul style="list-style-type: none"> Free radicals, such as the OH and O₂⁻¹ radicals, are involved in signaling pathways in cells.* Some enzymes use free radicals to carry out essential reactions in the body  <p>RNR (an enzyme that converts ribonucleotides to deoxyribonucleotides)</p> <p>For example, a protein called ribonucleotide reductase (RNR) catalyzes an essential step in DNA synthesis and repair using a free radical species.</p>
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DNA image courtesy of the U.S.Department of Energy Genome Programs

* The **hydroxyl radical (OH)** and **superoxide (O₂⁻¹)** are highly reactive oxygen radicals that are byproducts of oxygen metabolism in the body. These molecules are essential for life due to their role in cell signaling processes. However, because they are highly reactive, the radicals also react with DNA, resulting in DNA mutations that can ultimately lead to cancer. We have enzymes in our body that can repair DNA damage to some extent, and antioxidants, including vitamins A, C, and E, “trap” radicals to help minimize unwanted radical reactions, such as with DNA.

Lewis structures for the OH and O₂⁻¹ radicals:



Example 2) from page 2 of Lecture 12 notes: Free radicals in biology

Nitric oxide (NO)

(note: Nitric oxide is NO, not to be confused with nitrous oxide, or happy gas, N₂O.)



Nitric oxide

- NO is an important cell-signaling molecule in humans. It is produced in the inner lining of blood vessels and signals for the surrounding smooth muscle to relax, resulting in increased blood flow and thus increased transport of oxygen to cells in the body.
- NO is a gas, which is extremely unusual for a signaling molecule.

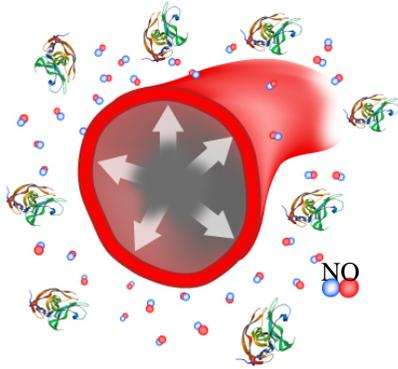


Figure by MIT OpenCourseWare

- NO diffuses freely across cell membranes. The illustration shows NO molecules signaling for the smooth muscle surrounding blood vessels to relax, resulting in vasodilation (increasing the diameter of blood vessels) and increased blood flow.
- As a *radical species*, NO has a short lifetime in the body, which makes it an ideal messenger molecule between adjacent cells.

You may be familiar with a drug that inhibits the breakdown of a downstream signaling molecule in the NO pathway...

Viagra inhibits the enzyme PDE5. PDE5 is responsible for breaking down the signaling molecule cGMP in the corpus cavernosum of the penis. When PDE5 is inhibited, higher levels of cGMP result in increased vasodilation (as shown in the schemes below) and thus increased blood flow to the penis.

