10.8: OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

OBJECTIVES

After completing this section, you should be able to

- identify organic reactions as being oxidations, reductions, or neither.
- rank given compounds in order of their oxidation level.

KEY TERMS

Make certain that you can define, and use in context, the terms below.

- oxidation
- reduction
- heteroatom

GENERAL REDOX REACTIONS

General chemistry courses describe oxidation and reduction - when a compound or atom is oxidized it loses electrons, and when it is reduced it gains electrons. Also, oxidation and reduction half reactions occur in pairs: if one species is oxidized, another must be reduced at the same time. Thus, the combination of an oxidation and a reduction half reaction is termed a 'redox reaction.' Most of the redox reactions you have seen previously in general chemistry typically involved the flow of electrons from one metal to another, such as the reaction between copper ion in solution and metallic zinc:

$$\mathrm{Cu^{+2}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{+2}(aq)}$$

$$\mathrm{Cu^{+2}(aq) + 2\,e^{-} \rightarrow Cu(s)}$$

Reduction

$$\mathrm{Zn(s) \rightarrow Zn^{+2}(aq) + 2\,e^{-}}$$

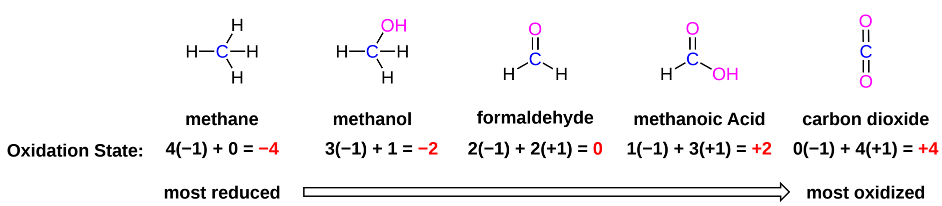
Oxidation

In order, to keep track of electrons in organic molecules an oxidation state formalism is used. Oxidation states do not represent the actual charge on an atom, but it will allow the number of electrons being gained or lost by a particular atom to be determined during a reaction.

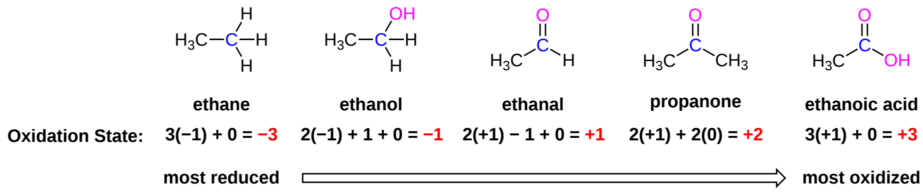
To calculate the oxidation state of a carbon atom the following rules are used:

1. A C-C bond does not affect the oxidation state of a carbon. So a carbon attached to 4 carbons has an oxidation state of zero.
2. Every C-H bond will **decrease** the oxidation state of the carbon by 1.
3. Each C-X bond will **increase** the oxidation state of the carbon by 1. Where X is an electronegative atom, such as nitrogen, oxygen, sulfur, or a halogen.

When looking at the oxidation states of carbon in the common functional groups shown below it can be said that carbon loses electron density as it becomes more oxidized. We'll take a series of single carbon compounds as an example. Methane (CH_4) is at the lowest oxidation level of carbon because is has the maximum possible number of bonds to hydrogen. Carbon dioxide (CO_2) is at the highest oxidation level because it has the maximum number of bonds to an electronegative atom.



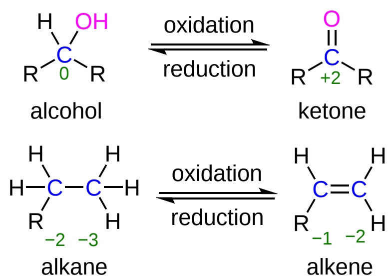
This pattern holds true for the relevant functional groups on organic molecules with two or more carbon atoms:



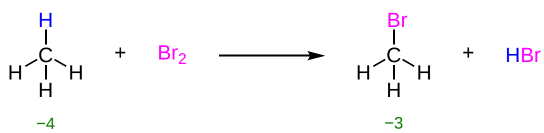
ORGANIC REDOX REACTIONS

It is important to be able to recognize when an organic molecule is being oxidized or reduced, because this information tells you to look for the participation of a corresponding redox agent that is being reduced or oxidized. If a reaction converts a compound to a higher oxidation level that is an oxidation. If it converts a compound to a lower oxidation level it is a reduction. If the oxidation level of the reactant does not change it is not a redox reaction.

Two examples of organic redox reactions are shown below. The conversion of an alcohol to a ketone is considered an oxidation because the oxidation level of the carbon increases from 0 to +2. This implies that the reaction would require an oxidizing agent. Likewise, the conversion of a ketone to an alcohol is a reduction and would require a reducing agent. The conversion of an alkane to alkene is an oxidation because the oxidation state on both carbons is increasing while the reverse reaction would be a reduction.

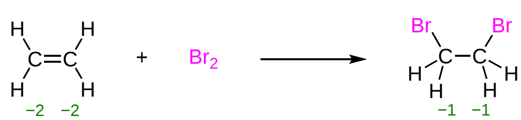


Now reaction previously discussed in this textbook can be considered to determine if they are in fact redox reaction. The free radical bromination of methane to bromomethane would be an oxidation because the oxidation level of carbon is raised from -4 to -3.

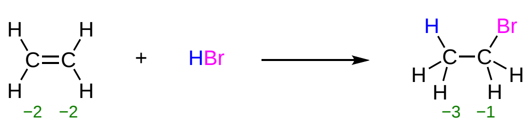


free radical halogenation: **oxidation**

The electrophilic addition of Br_2 to an alkene to provide a 1,2-dibromide is an oxidation because both carbons increase their oxidation level from -2 to -1. However, the electrophilic addion of HBr to an alkene to provide an alkyl halide is not a redox reaction because the overall oxidation state of carbons involved are not changed. One carbon has its oxidation level decreased from -2 to -3 while the other carbon's oxidation level is increased from -2 to -1. Overall, the change in oxidation level cancels out to leave an overall change of oxidcation level in the compound of 0.

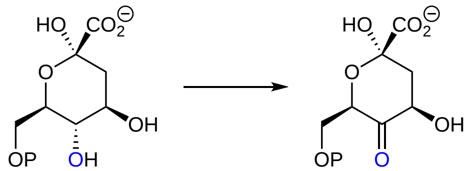


electrophilic addition of Br_2: **oxidation**

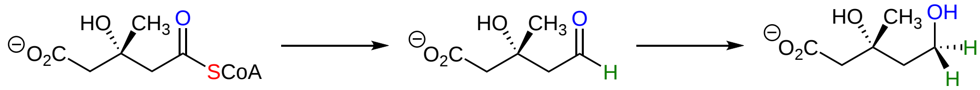


electrophilic addition of HBr: **not redox**

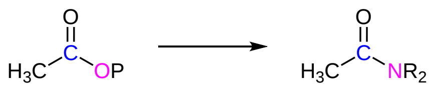
You should learn to recognize when a reaction involves a change in oxidation state in an organic reactant . Looking at the following transformation, for example, you should be able to quickly recognize that it is an oxidation: an alcohol functional group is converted to a ketone, which is one step up on the oxidation ladder.



Likewise, this next reaction involves the transformation of a carboxylic acid derivative (a thioester) first to an aldehyde, then to an alcohol: this is a *double* reduction, as the substrate loses two bonds to heteroatoms and gains two bonds to hydrogens.



An acyl transfer reaction (for example the conversion of an acyl phosphate to an amide) is *not* considered to be a redox reaction - the oxidation state of the organic molecule is does not change as substrate is converted to product, because a bond to one heteroatom (oxygen) has simply been traded for a bond to another heteroatom (nitrogen).



carbon is in same oxidation state: **not redox**

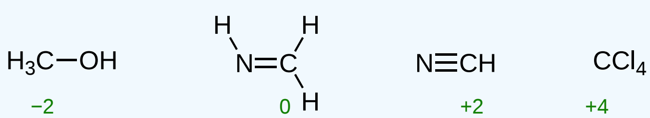
It is important to be able to recognize when an organic molecule is being oxidized or reduced, because this information tells you to look for the participation of a corresponding redox agent that is being reduced or oxidized- remember, oxidation and reduction always occur in tandem! We will soon learn in detail about the most important biochemical and laboratory redox agents.

Worked Example 10.8.1

Rank the following compounds in order of increasing oxidation level:

Answer

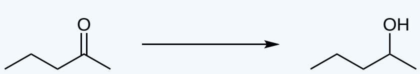
The easiest way to solve this problem is to calculate the oxidation level of the carbon in each compound. Remembering that hydrogens decrease the oxidation level by one, electronegative elements increase the oxidation level by one, and carbons do not change the oxidation level, the oxidation level of each carbon can be calculate. The carbon in CH_3OH has three bonds to hydrogens and one bond to oxygen so it oxidation level is 3(-1) + 1(+1) = -2. The carbon in HCN has one bond to hydrogens and three bonds to nitrogen so it oxidation level is 1(-1) + 3(+1) = +2. The carbon in CH_2NH has two bonds to hydrogens and two bond to nitrogen so it oxidation level is 2(-1) + 2(+1) = 0. The carbon in CCl_4 has zero bonds to hydrogens and four bonds to chlorine so it oxidation level is o(-1) + 4(+1) = +4. The compounds now can be listing in the following order of increasing oxidation level.



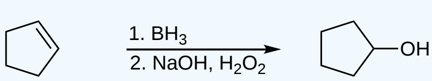
? EXERCISE 10.8.2

In each case state whether the reaction is an oxidation or reduction of the organic compound.

A -



B -



Answer

A – Reduction

B – Oxidation