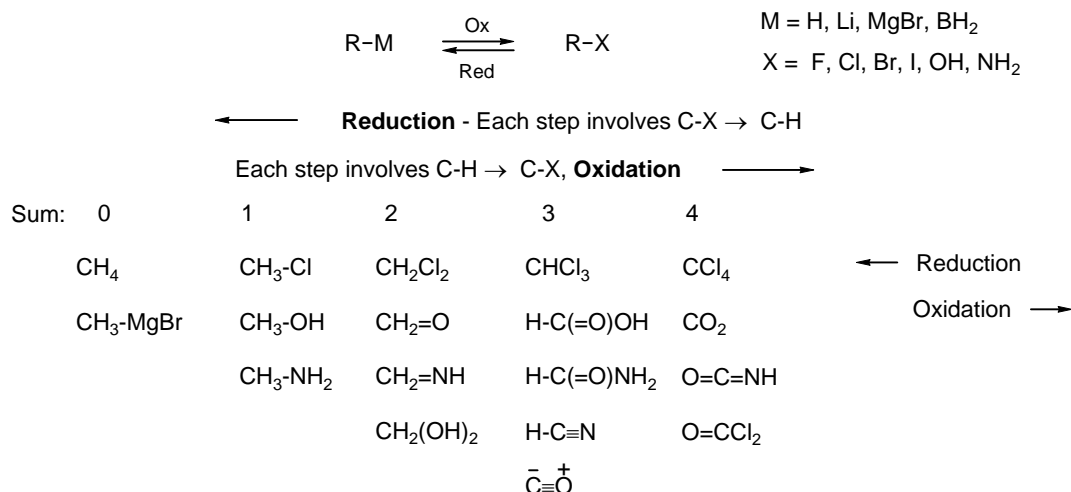
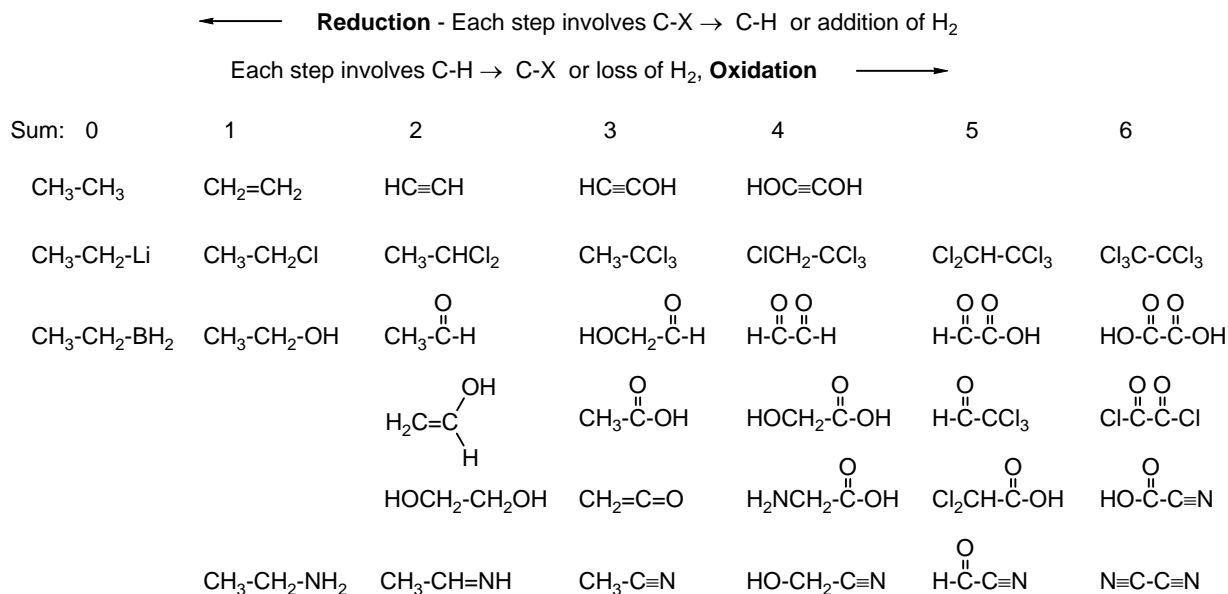


Oxidation State of Organic Molecules

The most reduced form of carbon is CH_4 , the most oxidized is CO_2 . Thus the oxidation state of a one-carbon fragment is unambiguous and defined by the number of C-H bonds that have been replaced by C-X bonds, where X = any electronegative element (see periodic table on previous page). Replacing C-H bonds by C-Metal bonds is not a redox process. A C=O double bond is equivalent to two C-O single bonds ($\text{C}(\text{OH})_2$).



When there are C-C bonds involved, the situation is more complicated. Now, in addition to replacement of C-H by C-X, oxidations can also involve the removal of H_2 by introduction of C-C and C-X double and triple bonds. To go left and right in the scheme below requires reduction and oxidation, respectively. Compounds in the same column are at the same oxidation state, and can be interconverted by nucleophilic substitutions (C-X by C-Y), electrophilic substitutions (C-H by C-M), additions or eliminations (of HX or MX fragments) and rearrangements.



The oxidation level of any carbon fragment can then be defined as the sum of the number of C-X bonds and number of π bonds to carbon (C=C, C \equiv C, C=O, C=N, C \equiv N). Two molecules with the same number of carbons and the same sum are at the same oxidation state, and can, in principle, be interconverted without any redox chemistry, or by an equal number of reductions and oxidations.

Redox Reagents

M-X species are NOT redox reagents

H-Br, H-OH, H-NH₂, Na-Br, Li-NⁱPr, R₃Si-Cl

Addition or elimination of an M-X species is not a redox reaction

M = H, Li, MgBr, BH₂

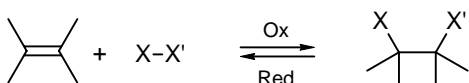
X = F, Cl, Br, I, OH, NH₂

X-X' Species are typically oxidizing agents

Br-Br, HO-OH, R₃N⁺-O⁻, RS-Cl, R₂N-Cl, RS-SR, etc

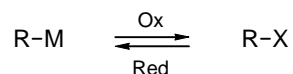
Addition of X-X' to a double bond is an **oxidation**

Elimination of X-X' to form a double bond is a **reduction**



Conversion of M to X is Oxidation

Conversion of X to M is Reduction



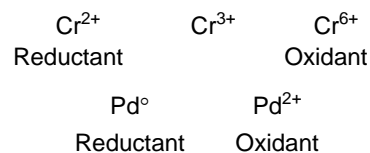
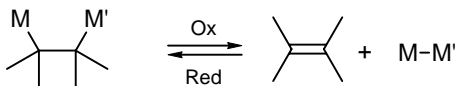
Transition metals are more complicated - each one has a favorite redox resting place. For all metals the lower oxidation states are reducing agents. Some elements (among them Cr, Ru, Mn, Os) have accessible higher oxidation states which behave as oxidizing agents.

M-M' Species are typically reducing agents

H-H, R₂B-H, R₃Sn-H, (Li-Li)_n, R₂B-BR₂, etc

Addition of M-M' to a double bond is a **reduction**

Elimination of M-M' to form a double bond is an **oxidation**



Reagents by Redox and Acid/Base Classes

Oxidizing Agents:

Free Radicals:

Cl·, Br·, I· (Cl· and Br· both add and abstract H)

Compounds with O-O bonds:

PhC(=O)OOC(=O)Ph, tBuOOtBu (free radical initiators)

O₃, RCO₃H, H₂O₂, O₂

Halogen molecules and related species:

Cl₂, Br₂, I₂, Cl-OH, Br-OH (add to π bonds)

Metals in high valence states:

KMnO₄, CrO₃ (and other Cr(VI) reagents), OsO₄, NaO₄, MnO₂, Fe(III), Cu(II), Ag(II)

Reducing Agents:

Hydrogenation:

H₂/catalyst (transition metals, esp. Pd, Pt, Ni)

Metals:

K⁰, Na⁰, Li⁰, Mg⁰, Zn⁰

Hydride Donors:

BH₃, LiAlH₄, NaBH₄, Li⁺ HAl(O^tBu)₃, Na⁺ BH₃CN

Inorganic Reducing Agents:

Bisulfite (NaHSO₃), Hypophosphorous acid (H₃PO₂), Thiosulfate (Na₂S₂O₃)

Nucleophiles/Bases:

Anionic

Carbon Centered: RLi, RMgX, R₂CuLi, N≡C:⁻

Nitrogen Centered: iPr₂N⁻Li⁺, H₂N⁻M⁺, N₃⁻

Oxygen Centered: RO⁻, HO⁻, CH₃C(=O)O⁻

Sulfur Centered: RS⁻, N≡C-S⁻

Halogens: Cl⁻, Br⁻, I⁻

Neutral

R₃N, H₃N, ROH, H₂O

Acids:

Mineral Acids:

HClO₄, H₂SO₄, HNO₃, HCl, HBr, HI, H₃PO₄

Strong Organic Acids:

RSO₃H, CF₃CO₂H

Carboxylic Acids:

RCO₂H

Weaker Organic Acids:

H-C≡N, ROH

Basicity, nucleophilicity, and reducing power do tend to go together; electrons are given up in all three cases. Good nucleophiles like I⁻ and RS⁻ can give up one electron to an easily reduced compound as well as act as nucleophiles (making Y-C bonds). In the same vein, acidity and oxidizing power are related. Some strong acids like HClO₄, HNO₃, and H₂SO₄ can oxidize compounds as well as protonate them.