Oxidation State of Organic Molecules

The most reduced form of carbon is CH₄, the most oxidized is CO₂. Thus the oxidation state of a one-carbon fragment is unambiguous and defined by the number of C-H bonds that have been replaced by C-X bonds, where X = any electronegative element (see periodic table on previous page).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 (C(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 H₂ 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 \( \pi \) bonds to carbon (C=C, C≡C, C=O, C≡N, C=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**

\[ \text{H–Br, H–OH, H–NH}_2, \text{Na–Br, Li–N’Pr, R}_3\text{Si–Cl} \]

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

**X–X’ Species are typically oxidizing agents**

\[ \text{Br–Br, HO–OH, R}_3\text{N–O, RS–Cl, R}_2\text{N–Cl, RS–SR, etc} \]

Addition of X–X’ to a double bond is an oxidation

Elimination of X–X’ to form a double bond is a reduction

**M–M’ Species are typically reducing agents**

\[ \text{H–H, R}_3\text{B–H, R}_3\text{Sn–H, (Li–Li), R}_2\text{B–BR}_2, \text{etc} \]

Addition of M–M’ to a double bond is a reduction

Elimination of M–M’ to form a double bond is an oxidation

\[ \text{M} + \text{X–X’} \xrightarrow{\text{Ox}} \xleftarrow{\text{Red}} \text{X} + \text{X’} \]

\[ \text{M} + \text{M’} \xrightarrow{\text{Ox}} \xleftarrow{\text{Red}} \text{M–M’} \]

**Conversion of M to X is Oxidation**

**Conversion of X to M is Reduction**

\[ \text{R–M} \xrightarrow{\text{Ox}} \text{R–X} \]

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.

\[ \text{Cr}^{2+}, \text{Cr}^{3+}, \text{Cr}^{6+} \]

Reductant Oxidant

\[ \text{Pd}^0, \text{Pd}^{2+} \]

Reductant Oxidant

\[ \text{M} = \text{H, Li, MgBr, BH}_2 \]

\[ \text{X} = \text{F, Cl, Br, I, OH, NH}_2 \]
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, NaIO₄, MnO₂, Fe(III), Cu(II), Ag(II)

**Reducing Agents:**
- Hydrogenation:
  - H₂/catalyst (transition metals, esp. Pd, Pt, Ni)
- Metals:
  - K⁺, Na⁺, Li⁺, Mg⁺, Zn⁺
- Hydride Donors:
  - BH₃, LiAlH₄, NaBH₄, Li⁺ HA⁻(O⁻Bu)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, H₂PO₄
- 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.