Oxidation and Reduction in Organic Chemistry

The previous sections have discussed substitution and elimination reactions of alcohols and their derivatives. These reactions have much in common with the analogous reactions of allyl halides. Now we turn to a different class of reactions: oxidations. Oxidation is a reaction of alcohols that has no simple analogy in allyl halide chemistry.

A. Oxidation Numbers

In organic chemistry, whether a transformation is an oxidation or a reduction is determined by the oxidation numbers of the reactants and products. The calculation and use of oxidation numbers is a "bookkeeping" process that involves three steps. After glancing over these steps, read carefully through Study Problem 10.2, which gives an example of the entire process.

1. Assign an oxidation level to each carbon that undergoes a change between reactant and product by the following method:
   a. For every bond from the carbon to a less electronegative element (including hydrogen), and for every negative charge on the carbon, assign a +1.
   b. For every bond from the carbon to another carbon atom, and for every unpaired electron on the carbon, assign a zero.
   c. For every bond from the carbon to a more electronegative element, and for every positive charge on the carbon, assign a -1.
   d. Add the numbers assigned under (a), (b), and (c) to obtain the oxidation level of the carbon under consideration.

2. Determine the oxidation number $N_{ox}$ of both the reactant and product by adding, within each compound, the oxidation levels of all the carbons computed in Step 1. Remember: consider only the carbons that undergo a change in the reaction.

3. Compute the difference $N_{ox(\text{product})} - N_{ox(\text{reactant})}$ to determine whether the transformation is an oxidation, reduction, or neither.
   a. If the difference is a positive number, the transformation is an oxidation.
   b. If the difference is a negative number, the transformation is a reduction.
   c. If the difference is zero, the transformation is neither an oxidation nor a reduction.
Decide whether the following transformation is an oxidation, a reduction, or neither.

$$\begin{align*}
\text{isopropyl alcohol} & \quad \text{HO}\quad \text{CH} \quad \text{CH} \quad \text{H} \\
\quad \text{H} & \quad \text{CH} \quad \text{CH} \quad \text{O} \\
\text{acetic acid} & \quad \text{H} \quad \text{C} \quad \text{CH} \quad \text{O}
\end{align*}$$

Solution

**Step 1**

For both the reactant and the product, compute the oxidation level of each carbon that undergoes a change. Since the two methyl groups are unchanged, do not assign oxidation levels to these carbons. Only one carbon is changed. For this carbon, $-1$ is assigned for each bond to hydrogen (Rule 1a); $0$ is assigned for each bond to another carbon (Rule 1b); and $-1$ is assigned for each bond to oxygen (Rule 1c). Add the resulting numbers (color).

Reagent:

\[\begin{array}{c}
0 \\
\text{CH}_3 \quad \overset{\text{H}}{\quad \text{C} \quad \text{H}} \\
\text{CH}_2 \\
\end{array}\]

Product:

\[\begin{array}{c}
0 \\
\text{CH}_3 \quad \overset{\text{O}}{\quad \text{C} \quad \text{CH}_3} \\
\text{CH}_2 \\
\end{array}\]

Sum: $0 + 0 + (-1) = (-1) = 0$

Sum: $0 + 0 + (+2) = +2$

Notice that the $\text{C} \quad \text{O}$ double bond in the product acetone is treated as two bonds, each receiving a $-1$ for a total of $+2$ for the double bond.

**Step 2**

Add the oxidation levels for each carbon that changes to determine the oxidation number. Because only one carbon changes in Eq. 10.24, the oxidation level of this carbon, computed in Step 1, is the only one to be considered. Hence, $N_{\text{rat}}$ (reactant), the oxidation number of the reactant, isopropyl alcohol, is $0$. Similarly, $N_{\text{pro}}$ (product), the oxidation number of the product, acetone, is $+2$.

**Step 3**

Compute the difference $N_{\text{pro}}$ (product) $- N_{\text{rat}}$ (reactant), which is $+2 - 0 = +2$. Because this difference is positive, the transformation of isopropyl alcohol to acetone is an oxidation.

Notice that oxidation numbers are calculated for only the organic starting material and the corresponding product. The other reactant (H$_2$CrO$_4$ in Study Problem, 10.2) are not involved in the calculation.

Verify that the acid-catalyzed hydration of 2-methylpropene is neither an oxidation nor a reduction.
Solution  First, write the structures involved in the transformation:

\[ \text{2-methylpropane} \quad \text{tert-butyl alcohol} \]

\[ \begin{align*}
    \text{H}_2\text{C} & \quad \text{H}_3\text{C} \\
    \text{C} & \quad \text{C} \\
    \text{==CH}_2 & \quad \text{==CH}_3 \\
    \text{H}_2\text{C} & \\
\end{align*} \]

The oxidation number of the organic reactant, 2-methylpropane, is \(-2\):

\[ N_{ox} = \text{oxidation number} = \text{initial oxidation number} + \text{change in oxidation number} = -2 \]

The oxidation number of the organic product, tert-butyl alcohol, is also \(-2\):

\[ N_{ox} = \text{oxidation number} = \text{initial oxidation number} + \text{change in oxidation number} = -2 \]

Notice that the oxidation level is computed for only the one methyl group that was formed as a result of the transformation. Because the oxidation numbers of the reactant and product are equal, the hydration reaction is neither an oxidation nor a reduction. The same conclusion, of course, applies to the reverse reaction, dehydration of the alcohol to the alkene.

Notice in Study Problem 10.3 that one of the carbons of 2-methylpropane is reduced and one is oxidized; however, the net change in oxidation number for the overall transformation is zero.

The methods described here show that the addition of Br₂ to an alkene is an oxidation (the change in oxidation number is \(+2\)):

\[ \text{Br} \quad \text{Br} \]

\[ \text{R} - \text{CH} = \text{CH} - \text{R} + \text{Br}_2 \rightarrow \text{R} - \text{CH} - \text{OH} - \text{R} \quad (10.25) \]

Thus, whether a reaction is an oxidation or reduction does not necessarily depend on the introduction or loss of oxygen. However, in most oxidations of organic compounds, either a hydrogen in a \(\text{C}-\text{H}\) bond or a carbon in a \(\text{C}-\text{C}\) bond is replaced by a more electronegative element, which may be oxygen, but which may also be another element such as a halogen.

Study Problem 10.3 shows that a process which involves introduction of an oxygen (or other electronegative element) at one carbon atom is not an oxidation if another carbon atom is reduced at the same time. That is, the oxidation state of a molecule is determined by the sum of the oxidation states of its individual carbon atoms.
The oxidation-number formalism can also be used to relate organic oxidations and reductions to the definition of oxidation and reduction that you may have learned in general chemistry. An oxidation is a transformation in which electrons are lost, and a reduction is a transformation in which electrons are gained. To see how oxidation numbers are related to the loss or gain of electrons, consider the transformation of ethanol to acetic acid.

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}==\text{OH}
\]

\[
(10.28)
\]

The change in oxidation number for this transformation is +4 (confirm this); hence, this is an oxidation. Let's now view this transformation in another way by writing it as a balanced half-reaction that shows the loss of electrons. This process involves three steps:

1. Use \(H_2O\) to balance missing oxygen.
2. Use proton (that is, \(H^+\)) to balance missing hydrogen.
3. Use "dummy electrons" to balance charges.

This process is illustrated in Study Problem 10.4.

Write the transformation of Eq. 10.28 as a balanced half-reaction.

**Solution** First, balance the extra oxygen on the right with a water on the left:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C}==\text{OH} + \text{O}_2
\]

(10.27a)

Next, balance the extra hydrogen on the left with four protons on the right:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C}==\text{OH} + 4\text{H}^+
\]

(10.27b)

Finally, balance the extra positive charge on the right with "dummy electrons" so that the charges on both sides of the equation are equal:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C}==\text{OH} + 4\text{H}^+ + 4e^-
\]

(10.27c)

The result is the balanced half-reaction.

According to this half-reaction, four electrons are "lost" from the ethanol molecule when acetic acid is formed. Of course, electrons really aren't lost, because a corresponding number of electrons are "gained" by the species that brings about the oxidation. Nevertheless, on the basis of this half-reaction, it can be said that the oxidation of ethanol to acetic acid is a four-electron oxidation. This type of terminology is frequently used in biochemistry.

Recall now that the change in oxidation number for the ethanol-to-acetic acid transformation is +4. Notice the correspondence between the change of oxidation number (+4) and the "electrons lost" (+4) in the corresponding balanced half-reaction. This correspondence is general. That is, the change in oxidation number is equal to the number of electrons lost or gained in the corresponding half-reaction.
B. Reduction of Nitro Compounds

Nitro compounds can be reduced to amines under a variety of conditions. The nitro group is generally reduced easily by catalytic hydrogenation:

\[
\text{NO}_2 + \text{H}_2 + \text{Pd/C} \rightarrow \text{NH}_2
\]

(97% yield)  (23.60)

1,2-dimethoxy-4-nitrobenzene

An older but effective method for reducing the nitro group is the reduction of aromatic nitro compounds to primary amines with finely divided metal powders and HCl; iron or tin powder is frequently used.

\[
\text{NO}_2 + \text{SnCl}_2 \text{ or FeCl}_2 \rightarrow \text{NH}_2 + \text{Sn}^2+ \text{ or Fe}^2+ \text{ salts}
\]

(97% yield)  (23.61)

1-bromo-3-nitrobenzene

In this reaction, the nitro compound is reduced at nitrogen, and the metal, which is oxidized to a metal salt, is the reducing agent. Although the methods shown in both Eqs. 23.60 and 23.61 also work with aliphatic nitro compounds, they are particularly important with aromatic nitro compounds as methods for introducing an amino group into an aromatic ring.

In view of the utility of lithium aluminum hydride (LiAlH₄) and sodium borohydride (NaBH₄) as reducing agents for other compounds, it is reasonable to ask what happens when nitro compounds are treated with these reagents. Aromatic nitro compounds do react with LiAlH₄, but the reduction products are aminobenzenes (Sec. 23.108), not amines.

\[
\text{NO}_2 + \text{LiAlH}_4 \rightarrow \text{NH}_2
\]

(23.62)

Nitro groups do not react at all with sodium borohydride under the usual conditions.

Hence, LiAlH₄ and NaBH₄ are not useful in forming aromatic amines from nitro compounds.

Problem 23.31

Outline syntheses of the following compounds from the indicated starting materials:

(a) p-idoanisole from phenol and any other reagents

(b) m-bromoanisole from nitrobenzene