OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

OXIDATION STATE

Determination of oxidation state in simple inorganic compounds is usually an easy problem - the oxidation state of all but one of the elements in the compound is known and the remaining element can be determined by difference, since the sum of all oxidation numbers must be zero. For example, in $KMnO_4$, potassium is always +1, each oxygen is -2 (for a total oxidation number of -8) and thus the manganese must be +7.

In organic compounds, the carbon atoms can have any oxidation state from -4 (e.g. CH_4) to +4 (e.g. CCl_4). If there is more than one carbon in the molecule, each needs to be calculated, and there are now several more unknown oxidation states than there are knowns to use in their determination. An useful solution to the problem can be generated by recognizing two important facts:

1. an absolute value for the oxidation state cannot be determined.
2. only the *changes* in oxidation state during a reaction are needed, so the absolute value isn't needed.

The approach described here calculates oxidation state in a consistent manner which always gives the correct oxidation state change for a reaction, and parallels the method used for $KMnO_4$ above.

1. Elements other than carbon have their normal oxidation state: H: +1, O: -2, halogens: -1, and as a consequence OH: -1. There are easily recognized situations where these elements are known to have other oxidation states: hydrides (H: -1) such as $LiAlH_4$, peroxides (O: -1) such as H_2O_2, or the elements (Cl_2, H_2, O_2: 0).

2. Pick out the particular carbon of interest, the one that is changed during the reaction. Assign an oxidation state of 0 to any and all carbons attached to it and ignore the rest of the molecule altogether. Calculate the oxidation state of the selected carbon as you would for an inorganic compound, using just the oxidation states of directly attached heteroatoms.

Examples:

		Attached atoms	Sum of oxn nos. of attached	Oxidation State of C
CH_3 C CH_3	C1	3H, 1C	3(+1) + 0 = +3	- 3
O	C2	2C, 1O	2(0) + (-2) = -2	+2
	C3	3H, 1C	3(+1) + 0 = +3	- 3
H				
CH_3 C CH_3	C1	3H, 1C	3(+1) + 0 = +3	- 3
OH	C2	2C, 1H, 1OH	2(0) + 1 + (-1) = 0	0
	C3	3H, 1C	3(+1) + 0 = +3	- 3

In a reaction where the ketone is converted to the alcohol, the only *change* in oxidation state occurs at the carbon with the oxygen; its oxidation state is *reduced* from +2 to 0, equivalent to addition of 2 electrons.

The same procedure can be used to determine the oxidation state of nitrogen which varies from -3 (NH_3) to +5 (HNO_3); it occurs in all its oxidation states in organic compounds and can participate in redox reactions.

BALANCING EQUATIONS

To use these computations to determine the amounts of reagents to perform the chemical reaction, use these oxidation state changes as you did for inorganic reactions; the electrons donated by the reducing agent must be equal to the electrons gained by the oxidizing agent. For example, $LiAlH_4$, has a normal Li: +1, Al: +3, and abnormal H: -1, and reacts to produce the following products (the water is added the acetone and $LiAlH_4$ react).

$$LiAlH_4 \;+\; CH_3\,\underset{O}{C}\,CH_3 \;+\; H_2O \;\text{---->}\; CH_3\,\overset{H}{\underset{OH}{C}}\,CH_3 \;+\; LiOH \;+\; Al(OH)_3$$

Li +1, Al +3, O -2 and the CH_3 s are unchanged by this reaction. Changed are C and H. The half reactions, balanced, are:

$$LiAlH_4 \;\text{--->}\; 4H^+ \;+\; 8e^- \;+\; Li^+ \;+\; Al^{++}$$

$$CH_3\,\underset{O}{C}\,CH_3 \;+\; 2e^- \;+\; 2H^+ \;\text{--->}\; CH_3\,\overset{H}{\underset{OH}{C}}\,CH_3$$

Each $LiAlH_4$ can reduce 4 acetone molecules. Multiply the second equation by 4 and add the two. Then add 4 OH^- to each side to make the reagents correct (water instead of H^+) and:

$$4\,CH_3\,\underset{O}{C}\,CH_3 \;+\; LiAlH_4 \;+\; 4\,H_2O \;\text{--->}\; 4\,CH_3\,\overset{H}{\underset{OH}{C}}\,CH_3 \;+\; LiOH \;+\; Al(OH)_3$$

For practice, convince yourself that conversion of an alkyl halide to a Grignard reagent reduces the carbon by 2 electrons, and balance the equation for oxidation of an alcohol to a ketone by chromic acid.

OTHER USES

This procedure described above can also be used to show that oxidation/reduction has *not* occurred, even when the oxygen content of a molecule changes. For example, addition of water to an alkene:

$$CH_2{=}CH_2 \;+\; H_2O \;\overset{H^+\ (\text{catalyst})}{\text{--->}}\; CH_3\text{-}CH_2OH$$

Oxidation states   -2 -2   -3 -1

In this case, the computation indicates a reshuffling of electrons within the molecule, making the two carbons different, but no overall oxidation. This should not be surprising, since water is not itself easy to oxidize or reduce (sodium metal can reduce it partially to H_2).