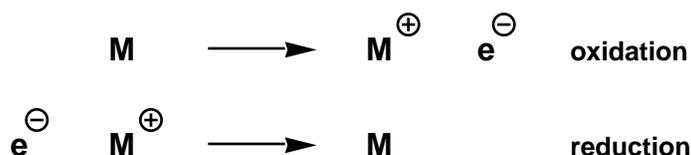
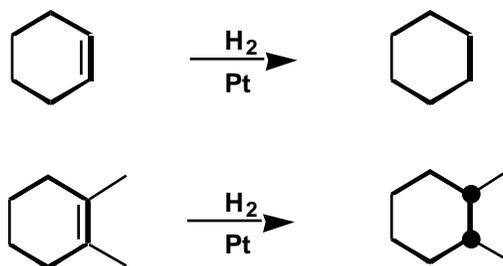


Text Related to Segment 12.01 ©2002 Claude E. Wintner

It is just a stone's throw away, so to speak, from the dichotomous relation acid/base to that of oxidation/reduction. Arguably the most familiar example of the oxidation/reduction concept is the relationship between a metal and a corresponding ion. We say of a metal when it is transformed into its ion that it has been oxidized. We say of an ion when it is converted to its parent metal that it has been reduced. Electrons must be donated *to* an ion, which thereby behaves as an acceptor, and thus as an *oxidizing agent*, in order that it may be reduced to its parent metal; conversely, electrons must be donated *by* a metal to an acceptor, in order that the metal, itself behaving as a *reducing agent*, may be oxidized to an ion. In this sense, the metal can function as a base (nucleophile) and the ion as an acid (electrophile):

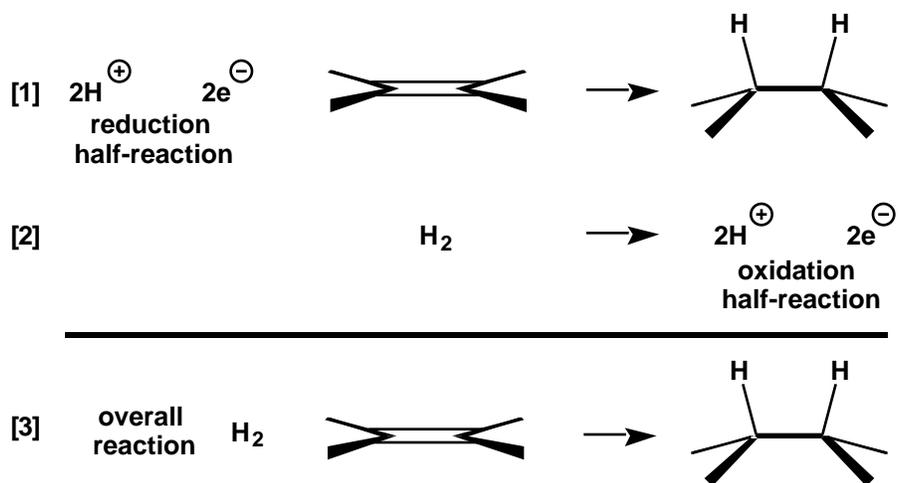


Conceptually perhaps the simplest reductive transformation in organic chemistry is the addition of the components of molecular hydrogen to a carbon-carbon double bond. Uncatalyzed, this reaction has a high kinetic activation barrier because of the great strength of the $\text{H}-\text{H}$ bond in molecular hydrogen; however, in the presence of a variety of catalysts, for example, platinum, a change takes place in such a manner that two hydrogen atoms are added *to the same face* of the double bond. In the next segment we shall discuss the role of the catalyst and the faciality of the reaction. Here we are concerned only with the overall stoichiometry and with how to go about writing the reaction as a balanced equation.



cis addition of molecular hydrogen to olefins

To understand this transformation as a *reduction* of an ethene, one simply needs to write out the organic reactant and product (it must be known, or be given, what these are!) in a formal half-reaction (so called because it describes either a reduction without the corresponding oxidation, or vice-versa), as in [1] below. After the organic reactant is placed on the left side of the equation and the product on the right, the equation is balanced atomically, using only protons or water (the latter not being required for balance in the present instance). As a final step, electrical balance is achieved through the appropriate placement of electrons. If the electrons appear on the right (product) side, the equation is that of an oxidation (electrons are donated by the reactant); if — as in [1] — the electrons appear on the left (reactant) side, the equation is that of a reduction (electrons are accepted by the reactant). Note that the reduction half-reaction describes only what is happening to the ethene. At the same time, a "payment" must be made: molecular hydrogen formally is oxidized to protons, as in [2]. The sum of the two formal half-reactions then gives the observed overall reaction, as in [3]. It must be understood that we speak of the overall reaction as a reduction only because we are considering it from the perspective of its organic substrate; in fact, it is a reduction coupled with an oxidation — the oxidation of molecular hydrogen.



half-reactions and overall reaction for
ethene reduction by molecular hydrogen

As one further example of the usefulness and simplicity of this formalism for balancing redox half-reactions, we present, in stepwise fashion, a case of oxidation of an organic substrate — here the oxidation of a primary alcohol to a carboxylic acid:

