13.8: Green Chemistry and Industrial Ecology

Green chemistry has an essential role to play in the development of successful industrial ecosystems, especially in making industrial metabolism as efficient, nonpolluting, and safe as possible. A major advantage of the practice of green chemistry to reduce environmental impact is that, ideally, it is inherently safe and clean. By using nontoxic chemicals and processes that do not threaten the environment, green chemistry avoids posing threats to the people who practice it and to the surrounding environment. Of course, these are ideals that can never be completely realized in practice, but by having these ideals as goals and making constant incremental improvements, the practice of green chemistry can become increasingly safe, environmentally friendly, and sustainable. This reduces dependence upon the command and control measures that require constant vigilance to maintain. Rather than depending upon regulations imposed from the outside to maintain its safe operation, green chemistry is much more self-regulating.

As discussed in Chapter 2 and illustrated in Figure 2.3, **Green chemistry** can be defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. In Section 2.10, twelve principles of green chemistry were presented. Following the discussion of industrial ecology and sustainability at the beginning of this chapter, green chemistry is now covered in greater detail here. Most of the modern aspects of green chemistry are discussed in a review article on the subject.[1] The major aspects of green chemistry discussed here include the following:

1. Efficient use of matter with minimum production of wastes
2. Catalysis
3. Utilization of biological processes
4. Maximization of renewable raw materials
5. Green product design
6. Minimization or elimination of solvents, use of water where possible
7. Process intensification

Green chemistry gives prime consideration to the chemical reactions and processes by which chemicals are manufactured. One approach to making chemical synthesis greener is to use existing chemical synthesis processes but make the process itself safer and less polluting while also making the reagents required for it by greener processes. An example of the former might be to substitute a less volatile, less toxic solvent as a reaction medium for a chemical synthesis reaction. In some cases, a reagent may be made more safely by using biological processes for its preparation in place of chemical processes. A second general approach to making chemical preparations greener is to use different reagents for the synthesis that are safer and less likely to pollute.

The practice of green chemistry is largely applied to the synthesis of organic chemicals. The history of organic synthesis abounds with examples of processes that are emphatically not "green." One example that is sometimes cited is the synthesis beginning with explosive trinitrotoluene(TNT!) of phloroglucinol, a chemical used in relatively small quantities in the fine chemicals industry. The synthesis began with oxidation by dichromate (a carcinogenic substance) in fuming sulfuric acid (a highly corrosive material that causes horrid lesions to skin) followed by reduction with iron in hydrochloric acid and heating to isolate the product. Although the quantity of product made was only about 100 tons per year, the process generated about 4,000 tons per year of solid waste containing $Cr_2(SO_4)_3$, NH_4Cl, $FeCl_2$, and $KHSO_4$. Clearly, this was not an environmentally friendly process and a major objective of green chemistry has been to find substitute pathways for synthesis such as this one.

Several key parameters are calculated in quantifying green chemistry. As discussed in Section 2.6, one of these is **atom economy** defined as the fraction of reactant material that actually ends up in final product. The higher the atom economy — ideally 100% — the greener the process. Oxidation, in organic synthesis the introduction of oxygen onto organic molecules, that uses various **oxidants** is an important process in synthesis. Oxidants are rated according to **oxygen availability**, the percentage of the mass of the oxidant molecule that is available oxygen, here represented as {O}. Theoretically, the molecule with the greatest oxygen availability is molecular O_2 rated at 100% (in practice one of the two O atoms usually ends up as water, H_2O). Hydrogen peroxide, H_2O_2, adds oxygen to an organic molecule, represented as "R", according to the reaction,

$$H_2O_2 + R \rightarrow R(O) + H_2O \tag{13.8.1}$$

Since the O atom is 47% of the mass of H_2O, the oxygen availability of hydrogen peroxide is 47%. When ozone acts as an oxidant by donating one of its three O atoms,

$$\mathrm{O_3 + R \rightarrow R(O) + O_2} \tag{13.8.2}$$

its oxygen availability is 33.3%, the percentage of the O_3 molecule that is one O atom.

For reduction, usually the addition of H atoms to a molecule, the concept of **hydrogen availability** may be used. When lithium hydride, molecular mass 7.94, is used as a reducing agent as in the synthesis of silane,

$$\mathrm{SiCl_4 + LiH \rightarrow SiH_4 + 4\,LiCl} \tag{13.8.3}$$

all of its hydrogen is used and its hydrogen availability is 12.6% which (because of the low atomic mass of Li, hence the low formula mass of LiH) is the highest hydrogen availability of all the metal hydrides.

The Presidential Green Chemistry Challenge Awards

The U.S. Presidential Green Chemistry Challenge Awards, administered by the Environmental Protection Agency with partial sponsorship by the American Chemical Society, are made annually to recognize efforts to reduce hazards and wastes from chemical processes and to help meet pollution prevention goals. The 77 winners of these awards since 1995 are estimated to have eliminated 97 million kg of hazardous chemicals from use, prevented the release of 26 million kg of greenhouse-warming carbon dioxide to the atmosphere, and saved 80 million liters of water. The 2010 awards included the following

• The development of genetically engineered microorganisms that can convert CO_2 to higher alcohols with more than 2 C atoms that have a lower percentage of oxygen and are more hydrocarbon-like than ethanol, therefore more useful as fuels and chemical feedstocks.

• The design of a biomaterials refinery as a substitute for a petroleum refinery that uses transgenic microorganisms to convert sugars to hydrocarbon alkanes and alkenes , long-chain fatty acids, and fatty esters

• The development of a process to use hydrogen peroxide to oxidize propylene to propylene oxide, one of the most widely used organic chemical feedstocks, using an approach that reduces capital costs, energy use, and wastewater generation.

• Alterations in the synthesis of sitagliptin, the active ingredient in Merck's Januviatype 2 diabetes drug. Sitagliptin is a chiral β-amino acid and the improved approach to its synthesis uses a genetically engineered transaminase enzyme to convert a precursor ketone to the desired product with increased yield, fewer production steps,and less overall waste.

• Development of a slow-release tablet form of insecticidal spinosad that makes it useful for mosquito control in aquatic environments where biodegradation of spinosad had been a problem with earlier forms of the insecticide