

13.9: Predicting and Reducing Hazards

The reduction of hazards from chemical processes was discussed Chapter 2, Section 2.7, “Reduction of Risk: Hazard and Exposure.” The conventional approach to making chemical processes less dangerous to workers and less harmful to the environment has emphasized *exposure reduction*. In the arena of worker safety, this has involved measures such as wearing protective gear to prevent contact with hazardous chemicals. For the environment as a whole it has consisted largely of “end-of-pipe” measures to prevent release of pollutants once they are generated.

In contrast to exposure reduction, green chemistry relies upon **hazard reduction**. The first step in hazard reduction is to know what the hazards are and where they originate. Hazards may arise from the raw materials used, the media (solvents) in which chemical processes are carried out, catalysts that enable chemical reactions to occur, and byproducts. The direct hazards posed to workers in a chemical process fall into the two main categories of toxicity hazards and hazards associated with uncontrolled events such as fires and explosions.

Toxic substances are most logically classified according to their biochemical properties that lead to toxic responses. A useful means of relating toxic effects to the chemical nature of toxic substances is through **structure activity relationships**, which use computer programs to find correlations between features of chemical structure, such as groupings of functional groups, and the toxicity of the compounds. As an example, organic compounds containing the N-N=O functional group are N-nitroso compounds, a family noted for members that cause cancer. Structural features that indicate a tendency to donate methyl (-CH₃) groups are also suspect because attachment of methyl groups to cellular DNA is a major mechanism in causing cancer. This hazard may be reduced by substituting alkyl groups with more carbons for the methyl group.

Three kinds of chemicals have a high priority in eliminating the toxicity hazards in green chemistry. The first such category consists of **heavy metals**, such as lead, mercury, and arsenic (a metalloid). These indestructible elements have a variety of toxic effects, such as impaired function of renal tubules in kidneys (cadmium), neurological damage (mercury), and inhibition of the production of ATP (see Chapter 7, Section 7.8, “Biochemical Processes in Metabolism”) A second major category of toxic substance that should be avoided in the practice of green chemistry consists of **lipid-soluble organics** that are not readily degraded. These compounds often consist of relatively high molecular mass organohalides, such as PCBs, and accumulate in lipid (fat) tissue. Released into the environment, these materials can undergo **biomagnification** as they move through a food chain. **Volatile organic compounds (VOCs)** constitute a third class of troublesome toxic substances. These are primarily hydrocarbons, such as heptane, and low-molecular-mass organohalides, such as trichloroethylene.

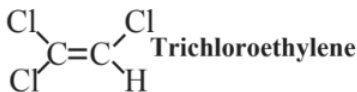
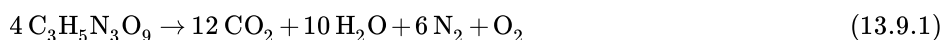


Figure 6.5) known to have caused liver cancer in workers exposed to the vapor in polyvinylchloride polymer manufacture.

Chemicals that pose hazards because of their potential to undergo destructive chemical reactions fall into several often overlapping categories. **Combustible** or **flammable** substances are those that are liable to burn vigorously and destructively in air or other sources of oxygen. Hydrocarbon solvents may closely resemble gasoline in their characteristics and are highly flammable. Adding to the hazards of such materials is their volatility, which enables them to form explosive mixtures of vapor in air. Destructive petroleum refinery fires fed by hydrocarbons can occur.

Whereas combustible substances are chemical *reducers*, another category of hazardous chemical substances consists of chemical **oxidizers** that provide sources of oxygen for the reaction of reducers (see Section 13.8). One such compound is ammonium perchlorate, NH₄ClO₄, a potent oxidizer used in rocket fuel. Many chemical synthesis procedures involve oxidation steps and a variety of chemical oxidizers are used for these steps. A fourth category of hazardous chemical substances are those that are **reactive**. Explosives are prime examples of reactive substances. One of the more treacherous explosives is nitroglycerin which undergoes the following reaction when it explodes.



This reaction shows that the nitroglycerin molecule actually contains an excess of oxygen because elemental oxygen is released when the nitroglycerin explodes. Some structural features of molecules are known to be associated with reactivity. One example is the close presence of oxygen and nitrogen on the same molecule, particularly where multiple nitrogen atoms are bonded together. A final category of hazardous chemical substances consists of those that are **corrosive**. In general, a corrosive substance is one that

attacks materials, including even human flesh. A more specific definition is that a corrosive substance is one that produces high concentrations of either H^+ ion (strong acid) or OH^- ion (strong base).

Often hazardous chemicals belong to two or even more of the categories outlined above. An example of such a substance is concentrated nitric acid, HNO_3 . In addition to its being a strong acid, this material acts as a source of oxygen, represented as $\{\text{O}\}$ in the reaction below:



Hazardous concentrated nitric acid is used in some chemical synthesis reactions in which an acidic oxidant is needed. Among the many other potentially hazardous strong oxidants used are permanganate (MnO_4^-) and oxygen-containing compounds such as potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.

The ideal way to deal with hazardous substances in the practice of green chemistry is to totally avoid making or using them. A laudable goal in principle, it is often impossible to completely avoid hazardous materials in practice. In cases where dealing with hazardous substances is necessary, every effort must be made to prevent their release, exposure to humans, or circumstances in which their hazards may be manifested.

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