Chapter 1: Green Chemistry

Green chemistry focuses on adapting chemical processes in order to achieve similar results to traditional reaction conditions, while reducing or eliminating human and environmental exposure to hazardous substances. As a discipline, green chemistry first gained traction in the early 1990s and today is an accepted and supported practice by government, industry, and educational institutions. Green chemistry is built around twelve principles, listed below.

A general formula for calculating the risk of a chemical is Risk = Hazard x Exposure. Traditional approaches focus only on minimizing the Exposure factor by using protective equipment, but protective equipment can fail. Green chemistry aims to minimize both terms, so even in the event of an accident, the inherent hazard of a chemical is not high enough to cause damage.

Although in some cases greener reagents appear to be more expensive, this is not always true – the costs for traditional, non-green reagents can often prove to be higher once deferred costs like waste treatment and safety equipment are factored in. The chemical industry is coming to realize this, and many large chemical companies are in the process of developing greener alternatives for large-scale synthesis that will save them large amounts of money in the long run. The Presidential Green Chemistry Challenge Award is presented each year to chemists and chemical companies who have developed reactions that simultaneously prevent pollution and bring significant economic benefits. Although progress is being made in adapting chemical industry to be greener, there is still a tremendous amount that remains to be accomplished.

1.1 The Twelve Principles of Green Chemistry

1. Prevention

This principle is perhaps the most important. It is better to prevent waste in the first place, rather than cleaning it up later. This can be achieved not just through following lab safety procedures to prevent spills, fires, and so forth, but also through planning ahead to make the most of chemical resources and minimize waste.

2. Atom Economy

Atom economy is given by the equation shown in Figure 1-1, and is a way of measuring the efficiency of the reaction: what percent of the reactants' total molecular mass is incorporated into the desired product, assuming 100% yield? The "MW of all reactants" term excludes things like catalysts, excess reagents, etc. – it looks only at the molecules that are used up in creating one molecule of product.

$$\text{Atom economy} = \frac{\text{MW of desired product}}{\text{MW of all reactants}}$$

Figure 1-1: The equation for atom economy.

This principle states that it is best to use all the atoms in a process, since the atoms that are not used end up as waste.

3. Less Hazardous Chemical Synthesis

Even a reasonably efficient chemical synthesis is undesirable if it uses very hazardous chemicals, since the safety risk is higher. Until a few decades ago, chemists have traditionally used whatever reagents were necessary for a given reaction, but over the last few decades many chemists have put effort into finding safer reagents to achieve the same goals.

4. Designing Safer Chemicals

This principle focuses on the product that is made, rather than the means of achieving it. If two chemicals are equally effective for a specific purpose, then the better choice is to use the less toxic one. A good example of this is pesticides: they are designed to be toxic specifically to pests, but at the same time their toxicity to other animals can be minimized.

5. Safer Solvents and Auxiliaries

Most chemical reactions are performed in solution. Traditionally, most organic reactions are done in organic solvents, many of which are toxic or pose other hazards such as flammability. However, there are many less toxic solvents available, including water. Even in cases where the reagents are not very soluble in nontoxic solvents, it is still sometimes possible to get them to dissolve by heating or the use of phase transfer catalysts.

6. Design for Energy Efficiency

This principle focuses on reducing the amount of energy required to synthesize a given amount of product. This can be achieved by minimizing the amount of electricity used for heating or cooling, or for powering other lab equipment such as stirrers.

7. Use of Renewable Feedstocks

A majority of the products we use on a daily basis are made from petroleum, in addition to the vast majority of fuel burned by our society. In fact, so many chemical feedstocks ultimately derive from petroleum that Dmitri Mendeleev (creator of the periodic table) once described it as "too valuable to burn." As petroleum use continues, feedstocks will continue to increase in price. This principle aims to reduce dependence on nonrenewable sources like petroleum, in favor of renewable sources. One example is polylactic acid (PLA), a compostable plastic derived from plant waste.

8. Reduce Derivatives

There are many times in a chemical synthesis where it is necessary to synthesize a derivative of a compound – a version containing groups which are not needed in the final product, but which allow the synthesis or purification steps to proceed more easily. One example of this is "protecting groups," which temporarily protect a functional group from being destroyed under reaction conditions that target another functional group in the molecule. However, these tend to lower atom economy, since they introduce atoms that are not incorporated into the final product but end up as waste. For many reactions that have traditionally required protecting groups, chemists are devoting research effort to finding alternatives that do not require them.

9. Catalysts

Catalysts are used to lower the transition energy for a reaction, allowing it to proceed faster and more selectively with less energy input. As an added bonus, catalysts are usually only needed in small quantities, rather than being used in stoichiometric amounts. In many cases, catalysts can even be recycled and used for many subsequent reactions.

10. Design for Degradation

This principle aims to create products that will perform their intended function for a set amount of time and then degrade into environmentally-friendly byproducts when they are disposed of. Many existing chemical products do not currently break down very quickly. Two examples are plastics, which take a very long time to break down in landfills, and some pharmaceuticals, which pass through the body unaltered and go on to pollute water systems.

11. Real-time Analysis for Pollution Prevention

Being able to monitor a reaction in real-time allows chemists to maximize yield and minimize byproducts. This can be done through many different techniques – TLC reaction monitoring is the most traditional for benchtop organic reactions, but there are many other methods that can be automatically run by machines so the reaction can be stopped at the best time.

12. Inherently Safer Chemistry for Accident Prevention

For any reaction, it is best to avoid highly reactive chemicals that could potentially cause accidents. The most widely known example of industrial chemical disasters is the accident that occurred in Bhopal, India in 1984. Water was accidentally allowed to flow into a tank containing methyl isocyanate gas, causing an explosion which released a large amount of methyl isocyanate into the surrounding area. As a result, four thousand people were killed and hundreds of thousands more were injured. If an alternative reaction had been developed that did not use this reagent, the risk of explosion and death would have been minimized.