## Green Chemistry

The term green chemistry describes an area of research arising from scientific discoveries about pollution and from public perception in much the same way as the identification and understanding of a deadly disease stimulate the call for a cure. The term, which was coined at the Environmental Protection Agency by Paul Anastas, represents the assumption that chemical processes that carry environmental negatives can be replaced with less polluting or nonpolluting alternatives. This supposition has been demonstrated to be true in a number of significant cases. We recognize that the environment is by constitution a vast array of interdependent life forms coupled to the internal or external chemistries that support them. We say the environment is polluted when, by inducing a change in a supporting chemistry, the practice of a human technology jeopardizes any life form that is recognized to be important to us. This definition of chemical pollution does not include all life forms because we must defend ourselves from certain organisms such as the bacteria that bring us fatal diseases. Green chemistry is a rational reaction to the alarm that pollution has engendered among visionaries such as Rachel Carson, who published her alert Silent Spring in 1962, government officials and scientists who evaluate and regulate against pollution, commentators who raise public consciousness about pollution, corporate executives who shoulder much of the responsibility for minimizing pollution, and concerned citizens.

Green chemistry presents those societies that have nurtured an ability to produce original chemistry with a new incentive for technological advancement. This incentive is the optimistic mission of developing technologies that do not detract from the richness or the possibilities of life by incrementally eliminating\_the sources rather than the symptoms of pollution (Anastas, 1994; Anastas and Williamson, 1996; Hancock and Cavanaugh, 1994). Because this infant field is currently being invented, it is appropriate for this entry to focus on a vision of its future. It will begin with a tangent to the main theme by probing a little into the reasons for pollution. We humans are an important component of the environment, and

many of our activities are environmentally harmless. In modern times, through science and its daughter technology, we have developed an ability to adapt the world about us to suit our desires as never before. We enjoy extraordinary benefits as a result. Consider, for example, the record of science in controlling or eliminating numerous crippling and life-threatening diseases: diphtheria, leprosy, poliomyelitis, rabies, rubella, smallpox, tetanus, typhus, typhoid fever, whooping cough, and many others. Without these benefits, many of the readers of this entry would never have been born, would have been maimed, or would have died at a young age. But our use of chemistry can carry significant environmental negatives. Chemistry in itself does not cause pollution. Rather, making a mess is a habit as old as mankind. The untidy mess the prehistoric child once surely made in a cave corner has become the present-day clutter of the modern child's bedroom. Throughout all the generations of human existence, the average child has resisted the parental demand to clean up. And one can guess that every imaginable rationalization has been presented at some time or another to support this resistance. However, the underlying reason is almost invariably the preoccupation of each child with his or her own immediate agenda. Few of us escape the fixation of looking first to our own desires and convenience by the time we reach adulthood. Few of us ever escape such habits. The messes we make as children move outside the home when we become adults. There they affect the neighborhood, the city, the region, the country, the continent, the oceans, the atmosphere, the entire planet.

With the power of science and technology comes a great responsibility: the responsibility not to pollute. When any of us with mastery over a powerful technology set our minds on a particular goal and, through naïveté and/or an obsession with our own objectives, jettison environmental considerations, we can do serious damage. We may pollute as individuals, or we may be in command of large enterprises or even huge nations, in which case our faults can result in massive environmental damage. Of an equally serious nature, we may simply create obstacles to change. The tendency to resist change aimed at achieving long-term environmental benefits may turn out to be our most serious flaw as a species. While excuses continue to be invented, the proportion of our population that is beginning to realize how much we have to change is growing substantially. As a result, our collective energy is being redirected wisely. This is especially true in the area of chemistry (Anastas, 1994; Anastas, 1996; Hancock and Cavanaugh 1994). Chemistry comprises such a large component

of modern technology that the development of foolproof green technologies is significantly a chemical enterprise.

One could give many examples of calamities wreaked on nature by humans throughout known history. In modern times, the real catastrophes usually result from the naive or irresponsible use of technology. When naïveté is the error, the environmental damage can arrive as an unexpected legacy of good intentions. The development of chlorofluorocarbons, called CFCs or Freon, in the search for the ideal refrigerant is such a case. Once released into the atmosphere, these highly stable molecules eventually reach the stratosphere where, under the bombardment of the high-energy radiation found there, they decompose to cause catalytic depletion of the stratospheric layer of ozone,  $O_3$  (see also OZONE DEPLETION). Stratospheric ozone shields the Earth from high-energy ultraviolet radiation emanating from the sun. Thus stratospheric ozone depletion could be detrimental to life, especially life forms that experience direct sunshine. Dealing with this problem has taught us that eliminating serious sources of planetwide environmental damage requires a reordering of priorities that can reach into many domains of human existence. In January 1989 the Montreal Protocol on Substances That Deplete the Ozone Layer went into effect. The protocol calls for reductions in production and consumption of several of the long-lived CFCs. This protocol, which has been ratified by many nations, coupled with the scientific development of stratospherically safer refrigerants and blowing agents and the reengineering of CFC technologies, provides our best signals to date that such a reordering-albeit imperfect, as a global reordering process is always likely to be-is not beyond our capability.

When irresponsibility is the error, one is left feeling resentful toward some person, group, enterprise, or system of administration whose culpability has been exposed. Each exposure reinforces our resolve that life, and not the fleeting desires of a single individual or group, should have sovereign power over the Earth. One is thankful for the strength of the individuals who have discovered and brought the case to the public eye and grateful for the free expression of democratic systems that make such exposures possible. Investigation, exposure, condemnation, and punishment of irresponsible environmental destroyers are a necessary and healthy process. But this process is only a component of our struggle to find the answer to one of the most fundamental questions we have ever had to deal with: "Is a large, technologically powerful human population sustainable on the Earth?" We exist in a tiny segment of the universe

The elements are the building blocks of our unique reality. Terrestrial things exist because of the special focus of chemistry—the bonds between elements and molecules that are thermodynamically stable in the peculiarly hospitable physical regime in which we find ourselves. Thus green chemistry may well be our most powerful tool in achieving the technological posture required for finding an encouraging answer to the question just posed.

One can already recognize a number of principles that are fundamental to green chemistry. First, genuine green chemistry is designed to eliminate pollution at its source. Thus its objective is never to imperil beneficial life forms. Second, chemists must master the scholarship of their particular field, and for most individuals, the demands of this mastery require a focused expertise. However, the Earth's environment is perhaps the most complex chemical system we know about, such that genuine mastery will likely elude most individuals. Thus many green chemistry projects will require multidisciplinary expertise best achieved by collaborations between or among appropriate specialists. Collaborations between industrial and academic partners are important to expedite the transfer of significant green products to the marketplace. To be successful, such collaborations require bipartisan flexibility as individuals in these two differently motivated cultures work together to advance green science. Governments could undoubtedly facilitate formation of more effective industrial-academic partnerships with some clever lawmaking. Third, the complexity of the environment requires us to take the long-term rather than the short-term view in a component of green research. Optimization of green research funding will require modifications in the criteria we utilize for the evaluation process. For example, we are not particularly good at evaluating strategic research projects in which challenging long-term goals are defined in the human imagination because the productivity factors we rate so highly in deciding which research to fund can easily overwhelm our more original risk-takers. In addition, environmental complexity can constrain any particular piece of green chemistry in profound ambiguity, which can only be eliminated with long-term multidisciplinary research.

The CFC story serves as an excellent example of the type of predicament we must be on the lookout for at all times. Ironically, the development of CFCs for refrigeration was an early exercise in green design. Refrigeration is a technological wonder that brings us extensive benefits. Since the beginning of refrigeration history in the first third of the nineteenth century and prior to the development of CFCs a hundred years later, different refrigerants had corroded seals and machinery; cooled inefficiently; decomposed; created serious health hazards, even causing death; and produced fires and explosions. Therefore, a search was on for a totally desirable refrigerant (Salas and Salas, 1992). Finally, in 1928, Frigidaire commissioned General Motors to produce the ideal refrigerant. A team led by Tom Midgely, Jr., developed the first CFC. For almost five decades, CFCs appeared to be the perfect refrigerants. It was not until 1974, when F. Sherwood Rowland and Mario J. Molina at the University of California at Irvine presented the hypothesis that CFCs destroyed ozone (Molina and Rowland, 1974), that the problem was first recognized. Joseph Farman discovered the Antarctic ozone hole in 1984 (Farman, Gardiner, and Shanklin, 1985), and the Montreal Protocol was developed at a meeting in Montreal in 1987. Now the CFCs are being replaced with the HCFCs, or hydrochlorofluorocarbons, which undergo more facile decomposition in the lower levels of the atmosphere (Manzer, 1994). Molina and Rowland, together with Paul Crutzen of the Max Planck Institute for Chemistry in Mainz, Germany, won the 1995 Nobel Prize in chemistry for their insights into the relationship between CFC and ozone. In 1970 Crutzen had pointed to the nitrogen oxides as strongly suspect ozonedestroying agents. The Nobel Prize citation from the Royal Swedish Academy of Sciences read: "The three researchers contributed to our salvation from a global environmental problem that could have catastrophic consequences."

For the reasons discussed above, green chemistry is taking an independent form as an amalgam of other chemical disciplines, especially organic, inorganic, and biological chemistry. The genesis of green chemistry as a mission-oriented scientific field in the modern sense might be traced to the official launch by the Environmental Protection Agency (EPA) in 1991 of the Alternative Synthetic Pathways for Pollution Prevention Grants Solicitation. Prior to this time, concern for the environment had helped to generate a large amount of research in specific areas, especially energy. Energy probably remains the most important single arena for green research, since consumption of fossil fuels underlies our entire technological lifestyle. Oil, coal, and natural gas are limited and nonrenewable; we are rapidly consuming the known resources. Our consumption is changing the composition of the atmosphere by adding carbon dioxide. The steady increase in ambient temperatures, called the greenhouse effect, has been attributed in part to this atmospheric CO<sub>2</sub> increase. Nuclear energy is an unpopular alternative because accidents can spread deadly toxic

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elements over state-size regions of the countryside. Thus greater reliance on solar energy is a safe and obvious answer to the current energy problems. Solar energy can be converted to storable chemical energy, and additional research is needed to find viable processes and to optimize existing ones. But solar energy can be used in other ways by chemists. For example, the use of renewable resources adapted through biocatalysis to replace fossil hydrocarbons as the primary material resource for large-usage, or commodity, chemicals is an exciting developing area that may already have yielded cost-effective technologies (Draths and Frost, 1994; Frost and Lievense, 1994). Here, genetic engineering is employed to adapt metabolic pathways in organisms so that the organism can convert a plant chemical such as the sugar D-glucose to large quantities of the desired commodity chemicals. D-glucose, derived from renewable plant resources and waste streams, is inexpensive and abundant. Solar energy can also be used to activate chemical reactions so that the environmentally undesirable chemical activators can be dispensed with (Kraus, Kirihara, and Wu, 1994).

Replacement processes that eliminate the use of toxic molecules or exclude the formation of toxic byproducts provide obvious examples of green chemistry. For example, the molecule phosgene  $(Cl_2C=O)$ was used as a toxic gas in warfare. It is heavier than air. When it was released on World War I battlefields under suitable weather conditions, it would flow across the field and into the enemy trenches. When inhaled, it attacks the lungs and mucous membranes of the victims, often fatally. The same reactivity responsible for its toxic properties has made it a widely used synthetic intermediate. However, great care must be employed because leakages cannot be tolerated. Thus new technologies are being invented to eliminate the use of phosgene (McGhee et al., 1996; Ono, 1996; Rivetti, Romano, and Delledonne, 1996). One example uses the safer alternative, dimethylcarbonate [(CH<sub>3</sub>O)<sub>2</sub>C=O] (Ono, 1996; Rivetti, Romano, and Delledonne, 1996), to replace phosgene in a solventless process for the production of polycarbonate  $[-OC_6H_4C(CH_3)_2C_6H_4OC(O)-]_n$ . This greened process also eliminates use of large quantities of the toxic solvent dichloromethane  $(CH_2Cl_2)$  (Komiya et al., 1996). Polycarbonate has an annual worldwide production of about 1 million tons, which is growing by about 10 percent per year.

It is easy to see why substitutes for acutely toxic molecules can improve chemical processes. But many other substances constitute chronic, as opposed to acute, health hazards. Chronic toxins accumulate slowly, and their deleterious effects become apparent

either after a long exposure period or a long time after the exposure has occurred. Many solvents are chronic toxins. Most synthetic chemistry occurs in solvents, which generally constitute a large component of the material employed in any process. Only a few of the major technological solvents are molecules found abundantly in nature. Consequently, living systems are unfamiliar with the unnatural solvents and have not evolved mechanisms for dealing with them. A number of solvents have been found to be carcinogenic (cancer-inducing). As a result they have been eliminated for most uses, and any ongoing use has been strictly regulated. Benzene  $(C_6H_6)$  and carbon tetrachloride (CCl<sub>4</sub>) are examples of carcinogenic solvents, but many toxic solvents such as dichloromethane are also being targeted for elimination (Komiya et al., 1996; see also MUTAGENS AND CARCINOGENS). Water is nature's principal solvent. Thus the substitution of unnatural solvents with water provides an opportunity to improve the environmental friendliness of a given process. Such a substitution is not as easy as it might sound, since changing an organic solvent for water will require a complete redesign of the system. In the process, one must be very careful. Water easily passes into most components of the environment, including living organisms, so it can carry soluble species throughout the environment with much greater ease than the organic solvent targeted for replacement. Therefore one must be sure that all products and by-products either are completely removed from the waste streams of a redesigned process or are harmless. Another abundant natural molecule is the gas CARBON DIOXIDE. When compressed to a liquid or above its critical point (T<sub>c</sub> = 31.1°C, P<sub>c</sub> = 1071 psi,  $\rho_c$  = 0.468 g/  $ml^{-1}$ ) to a supercritical fluid, carbon dioxide can be a nontoxic, nonflammable, inexpensive alternative to organic solvents (Morgenstern et al., 1996). The development of carbon dioxide as a solvent for synthetic chemistry is receiving considerable attention because of the advent of green chemistry (Donahue et al., 1996; Morgenstern et al., 1996). Since the solvent is extracted from the atmosphere, its use and eventual return to the atmosphere result in a net zero change in atmospheric CO<sub>2</sub>.

A molecule can pollute because it incorporates a toxic element. This class of pollutants is large. An example is tetraethyllead, an efficient antiknock agent that was once widely used in automobile gasolines. Its naive use resulted in an extensive distribution of highly toxic lead in the midst of human populations and beyond. Following scientific analysis of the many lead-induced health problems (Needleman, 1992), tetraethyllead usage has been significantly reduced, and much safer antiknock agents have been developed. Similarly, lead additives produce superior oil-based paints, but lead-free paint technologies have been invented and optimized as lead has been banned from paints in certain countries.

A process can also be "greened" by redevelopment that results in the use of fewer chemical reagents or solvents or less energy per unit transformation, or in the production of smaller quantities of waste products. The quest for efficiency has been called atom economy, and it is a reason why many chemists are approaching green chemistry by expanding the use of catalysis (Cusamano, 1992; Simmons, 1996). A catalyst, often in trace quantities, will speed up a chemical reaction while returning a higher selectivity at lower temperatures than is possible without the catalyst. Thus catalysts offer significant benefits to chemical processes. They can reduce the amounts of energy and chemicals needed, facilitate product separation, diminish the quantity of waste products, return unique selectivities, and even channel a chemical process away from toxic impurities. Quite often, catalysts contain elements that are rare, expensive, or toxic. Consequently many green projects are focused on catalyst substitutions.

Catalysts also can activate environmentally desirable reagents that would otherwise be unsuitable for a particular transformation. Thus they may allow the replacement of environmentally undesirable reagents that are in use only because desirable ones are ineffective. For example, the principal raw materials of chemical technology are petroleum and coal. Both consist primarily of carbon and hydrogen. Most useful chemicals also contain oxygen, and the chemical reactants that introduce oxygen into these petrochemicals are collectively called oxidants. The field of oxidant use, called oxidation chemistry, constitutes a huge component of technology. Many widely employed oxidation systems are not optimal for the environment. Either they rely on less than desirable oxidants, or catalysts are employed that decay quickly in use to create transition metal by-products, many of which are toxic. Often these by-products must be cleaned from waste streams at significant costs to achieve environmentally acceptable systems. Two abundant natural oxidants are oxygen (O2) and hydrogen peroxide  $(H_2O_2)$ . Both are inexpensive but are vastly underutilized because of their low kinetic reactivity. Thus activating these oxidants with catalysts is a frontier of reaction chemistry, particularly in the area of homogeneous oxidation, where all reacting species are dissolved in solution. Most homogeneous oxidants and oxidation catalysts are transition-metal compounds consisting of a metal ion attached to LIGANDS, the other atoms or groups of atoms attached to the metal ion. Most ligands are degraded by strongly oxidizing metal ions with loss of the catalyst's activity, which is the major reason that there are numerous inadequately solved (or unsolved) oxidation processes. As a result, certain green programs are focused on obtaining oxidatively robust ligand systems for nontoxic catalysts that will expand the use of hydrogen peroxide and oxygen (Collins, 1994; Ellis, Lyons, and Myers, 1990).

But success in producing robust ligand systems is allowing broader strategic goals to be envisioned that were inconceivable until quite recently (Collins, 1994). It is important to recognize that technological chemistry and natural chemistry are largely dissimilar in the following fundamental way. While chemists use the entire periodic table to achieve the broad range of selectivity they desire, they practice a relatively simple form of reagent design. In contrast, nature uses a limited number of elements, so that it often requires an extraordinarily sophisticated reagent design to achieve broad reactivity objectives. Nature's catalysts, enzymes, are much larger molecules than the homogeneous catalysts used by chemists. The size and complexity of enzymes are key to their ability to orchestrate a series of reactivity-directing features in both time and space to achieve the targeted selectivity. While catalyst discoveries can reveal complex systems, chemists design catalysts around the relatively simple focus of controlling just one reaction to achieve a targeted selectivity. This difference contributes to the use in technological chemistry of elements that are unfamiliar in nature and consequently toxic to living organisms. By obtaining robust ligands, chemists are compensating for the absence in their constellation of the repair and replacement mechanisms of life and are positioning themselves to develop enzymelike multifunctional reagents and catalysts based on nontoxic elements. The effort invested in developing such complex systems makes sense only if the targeted reagent is stable in the long term (Collins, 1994). Of course, one must also be very careful to ensure that the molecular multifunctional reagents are not toxic by virtue of their structure.

In conclusion, green chemistry is a field that attempts to integrate the practical, scientific, and economic realities of a technologically advanced human population into a philosophical stance in which the benefit and sustainability of the rich array of life on Earth are given due importance. But science is only one essential component of optimizing technology with respect to the environment. Other essential components require fortitude by appropriate specialists.

In particular, interactions among the multitude of our cultures are complex, often unpredictable, and potentially irrational, so that showing that any particular form of pollution can be eliminated in one culture does not mean that all cultures can or will incorporate the innovation into their technology. For this and for many other reasons, it would appear that the race is on between our integrity backed by science and our egocentric tendency to overindulge ourselves in the extraordinary power given us by science and technology. The stakes are enormous. To the best of our knowledge, our world is just right for the bounteous life that is found here, and Earth is the only place in the universe where we know for certain that life does exist. What we might call "the environment" has a different reality in a black hole, where the elements have no existence as such; in outer space, where there is insufficient matter to construct and sustain something as complex as a living creature; and even on the neighboring planets, where the abundances of elements in states critical to life are not suitable and the flux of energy from the sun is too great or too small. Our intellectual gifts have given us science and technology and with them the custody of life, all life known to us. We have the power to nourish life and the power to destroy it. This responsibility is made even more daunting by the realization that the naive or irresponsible use of technology could unleash uncontrollable environmental forces that might deprive us of our ability to nourish life. Thus our only sensible options are to look ever more carefully for the messages the environment sends back to us about how we are treating it and to adjust our collective technologies and individual lifestyles to minimize or eliminate further environmental damage. The good news is that we are learning to do this in earnest across a number of our cultures. As a result, it is likely that science and economic activity will focus significantly on environmental enhancement, which is the positive side of the environmental protection coin and which may well be a healthy place for overindulgence that we have hardly begun to explore. As a key ingredient of our coming to terms with the realities of our existence, green chemistry is certain to become a very significant component of science in the decades to come.

See also ENVIRONMENT AND ATMOSPHERE.

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