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20 GREEN CHEMISTRY FOR A SUSTAINABLE FUTURE

20.1 INTRODUCTION

If one dates the beginnings of chemical industry as a significant economic force from approximately 1850, it is approximately 150 years old. During that time, and particularly during the last half century, this industry has grown to be a huge enterprise fulfilling a large number of human needs and serving to underpin advanced industrialized economies. Because of the potential of this industry to affect all segments of the environment, it can be argued that it is the most significant segment of the anthrosphere. Following the laws of conventional economics, the chemical industry has been directed toward producing more and higher value products at the lowest cost, as measured in conventional economic terms. However, particularly since about the World War II era, it has become increasingly obvious that the practice of industrial chemistry has other costs—environmental costs—not usually measured by the incomplete measures of conventional economics. Some of these costs, such as loss of crop production from the effects of air pollution, have been relatively easy to quantify. Other costs—no less real—have proven difficult to assign a monetary value. These are the costs of damage to the environment and human health resulting from the misuse of chemical processes and products.

In recognition of the environmental effects of the chemical industry and related enterprises, many laws have been passed and implemented throughout the world to regulate chemical processes and products. These laws have emphasized dealing with environmental problems after they have occurred, a “command and control” approach. Compliance with environmental laws over the last several decades has involved the expenditure of more than a trillion dollars worldwide. These laws have unquestionably had some positive effects upon environmental quality, have been effective in helping to save some species from extinction, and have improved human health and quality of life. However, necessary as it is, the regulatory approach to enhancing environmental quality has some definite deficiencies. Its effective implementation and maintenance have required legions of regulators and have resulted in

the expenditure of vast sums for litigation that could be better used directly to enhance environmental quality. In some cases the regulations have appeared to be petty and poorly cost effective.

A modern industrial society will always require regulations of various kinds to maintain environmental quality and even to ensure its continued existence. But, are there alternatives to some of the regulations? Most desirable are alternatives that help to ensure environmental quality by “natural,” self-regulating means. Since about 1990, it has become increasingly evident that, at least to a certain extent, there are alternatives for the chemical industry and associated enterprises through the practice of what has come to be known in the United States and several other countries as **green chemistry**.

What is green chemistry? Perhaps the most straightforward answer to that question is that we are still trying to find out. The term has somewhat different meanings to different people with different perspectives. One definition of green chemistry is “carry out chemical activities—including chemical design, manufacture, use, and disposal—such that hazardous substances will not be used and generated.”¹ It must be recognized that the use of hazardous substances is unlikely to ever be totally eliminated. The challenge is to use such substances in a manner that is safe and prevents their dispersal to the environment. With this in mind, green chemistry can be defined somewhat more broadly as *the sustainable exercise of chemical science and technology within the framework of good practice of industrial ecology such that the use and handling of hazardous substances are minimized and such substances are never released to the environment*. The inclusion of industrial ecology (see Chapter 19) in this definition carries with it a number of implications regarding minimum consumption of raw materials, maximum recycling of materials, minimum production of unusable byproducts, and other environmentally friendly factors.

A key aspect of green chemistry is **sustainability**. Ideally, green chemistry is self-sustaining for several reasons. One of these is economic because green chemistry in its most developed form is less costly in strictly monetary terms than chemistry the way it has been traditionally practiced. Green chemistry is sustainable in terms of materials because of its minimum efficient use of raw materials. And green chemistry is sustainable in terms of wastes, because it does not cause an intolerable accumulation of hazardous-waste products.

In implementing the practice of green chemistry, two often-complementary approaches are the following:

- Use existing chemicals, but make them by environmentally benign syntheses.
- Substitute chemicals made by environmentally benign syntheses for existing chemicals.

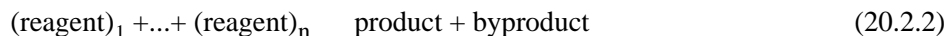
Both approaches need to be used. And both approaches challenge the ingenuity of chemists and chemical engineers to come up with innovative solutions to environmental problems arising from the chemical industry.

20.2 THE KEY CONCEPT OF ATOM ECONOMY

Although the yield of a product conventionally defined as the percentage conversion of a limiting reagent to the desired product may be quite high, or even reach 100%, the process may still produce large quantities of undesirable byproduct. Therefore, a much better measure of the degree to which a synthesis is consistent with the process of green chemistry is **atom economy** defined as follows:²

$$\text{Atom economy} = \frac{\text{Molecular mass desired product}}{\text{Total molecular mass of materials generated}} \quad (20.2.1)$$

The concept of atom economy can be illustrated in general by the reaction,



The ultimate in atom economy is achieved when there is no byproduct so that,



and all the reagents are contained within the product. Although this is often not achievable in practice, it is desirable to devise reaction schemes such that



One of the greater needs in chemical research today is the development of reactions for synthesis that have a high degree of atom economy.³

20.3 HAZARD REDUCTION

The practice of green chemistry requires constant efforts to reduce hazards from feedstocks, media, catalysts, and byproducts. Hazards may take a number of different forms. Among the most obvious of these are hazards from flammable or explosive reagents or media, particularly solvents. Materials may also present health hazards, such as the known human carcinogenicity of vinyl chloride used as a raw material in the manufacture of polyvinyl chloride polymers, or symptoms of peripheral neuropathy caused by exposure to light hydrocarbon liquids such as pentane.

Since hazardous substances manifest their hazards largely through their chemical reactions and characteristics, it is convenient to classify them chemically. Although the chemical variability of hazardous substances make such a classification system somewhat inexact, several categories can be defined based upon chemical behavior.⁴ These are the following:

- **Combustible** and **flammable** substances, strong reducers that burn readily or violently in the presence of atmospheric oxygen
- **Oxidizers** that provide oxygen for the combustion of reducers
- **Reactive** substances that are likely to undergo rapid, violent reactions, often in an unpredictable manner

- **Corrosive** substances that are generally sources of H⁺ ion or OH⁻ ion and that tend to react destructively with materials, particularly metals

Some hazardous substances fall into more than one of these groups, which increases the dangers that they pose.

Often the greatest concern with hazardous substances has to do with toxicity. Toxic substances are not so easy to classify in terms of chemical properties as are substances belonging to the classifications listed above. It is more appropriate to classify toxic substances on the basis of their biochemical properties. Of special use in making these classifications are **structure-activity relationships** that relate known structural features and functional groups to likely toxic effects.

Three kinds of hazardous substances stand out as candidates for reduction in the practice of green chemistry. The first of these consists of **heavy metals**, such as lead, mercury, or cadmium. As elements, these substances are indestructible. They have a wide range of adverse biological effects. Another category consists of **persistent, nonbiodegradable organic materials**, such as polychlorinated biphenyls, PCBs. Often not extremely toxic, these substances persist in the environment and exhibit a tendency to become magnified through biological food chains, adversely affecting organisms at or near the end of the food chain. The classic example of such compounds is insecticidal DDT, which caused reproductive problems for birds, such as falcons or eagles, at the top of the food chain. A third category of troublesome hazardous substances consists of **volatile organic compounds, VOCs**. These have been particularly prevalent in industrial settings because of their uses as solvents for organic reactions, vehicles in paints and coatings, and for cleaning parts. In the latter two applications, the most convenient means of dealing with these volatile materials was to allow them to evaporate, so that large quantities were simply discharged to the atmosphere.

Regardless of the kind of hazard posed by a substance, a major goal of the practice of green chemistry is to avoid having to deal with such substances in any way. Although this is an idealistic and largely unrealizable target in practice, having it as the ultimate goal serves as a good framework for the practice of benign and sustainable chemistry. Insofar as hazardous substances are concerned, the practice of green chemistry requires: (1) don't use them, (2) don't make them, and (3), if (1) and/or (2) cannot be avoided, never release hazardous substances to the environment.

20.4 FEEDSTOCKS

A crucial decision that must be made in implementing a process to manufacture a chemical or product is selection of **feedstock**. To the extent possible, the feedstock should place minimal demands on Earth's resources. It should be as safe as possible, and its acquisition and refining should be safe. In some cases the processes and reagents required to isolate an otherwise safe feedstock make its acquisition hazardous, such as in the use of highly toxic cyanide to remove low levels of gold from ore. Wherever possible, a feedstock should be *renewable*; for example feedstocks from biomass that can be grown repeatedly are often preferable to depletable petroleum feedstocks.

In a generalized sense, the overall process of obtaining a useful product from a feedstock, such as petroleum or biological materials, can be divided into the three categories shown in Figure 20.1. Both the petroleum and biological sources of potential feedstocks are relatively well known. For petroleum feedstocks, the technology for separation has been developed to a high degree of sophistication. The technologies for obtaining raw materials from plant sources, such as extraction of oils with solvents or separation of cellulose from lignin in wood, are well advanced. Because of the high degree of development of the petrochemical industry, the science of converting petroleum feedstocks to desired products is very well developed, but is less so in the case of biological feedstocks.

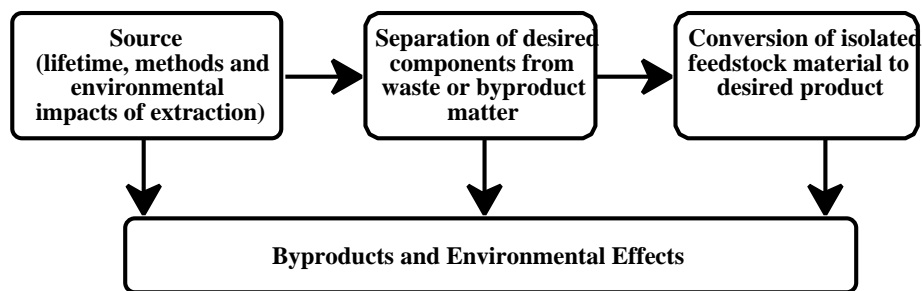


Figure 20.1 The three major steps in obtaining a feedstock and converting it to a useful product. Each of these steps has environmental implications and can benefit from the application of the principles of green chemistry.

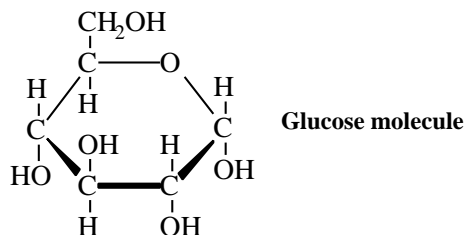
Biological Feedstocks

With some billions of tons of carbon fixed as biomass each year, there exists an enormous potential for the use of biological materials as feedstocks. The most obvious such material consists of wood from trees. Large quantities of cellulose are generated each year in the production of crops such as corn and wheat. Although a fraction of crop byproduct biomass should be returned to soil to maintain its condition as a growth medium for plants, there is a substantial excess that could be used as feedstock. Biological processes, particularly plant growth, produce a number of potentially useful biopolymers including, in addition to cellulose, hemicellulose, starch, lignin, and proteins. Plants are also useful sources of smaller molecules, including monosaccharides (glucose), disaccharides (sucrose), amino acids, waxes, fats, oils, and terpene hydrocarbons, including those used to make natural rubber. The potential of genetic engineering to produce plants that have high yields of feedstock chemicals could lead to the development of exciting new sources of biological feedstocks.

Potential feedstocks from biological sources tend to be more complex than those from petroleum. This offers the advantage of starting with a material in which much of the synthesis required to make a product has already been done by a living plant. Furthermore, many desired products have relatively high oxygen contents, and biological materials tend to contain bound oxygen. This can avoid the operation of converting a petroleum-based hydrocarbon feedstock to an oxygenated compound, which often requires severe conditions, hazardous oxidizing agents, and potentially

troublesome catalysts. In some cases, however, the complexity of biological feedstocks is a disadvantage because it is usually more difficult to convert a complex molecule to a significantly different one than it is to use a relatively simple feedstock.

Arguably the most important biological raw materials for chemical synthesis are carbohydrates produced by plants, including glucose, fructose, sucrose, and starch.



Carbohydrates, such as starch from corn grain and sucrose from sugar cane, are generated in high quantities by a number of plants. Furthermore, cellulosic wastes can be hydrolyzed to generate simple sugars that can be used in chemical synthesis. A major advantage of carbohydrates in chemical synthesis is their abundance of hydroxyl functional groups, as shown in the structure of glucose above. Such functionality provides sites for the attachment of other functionalities and for initiating chemical reactions leading to desired products. The inherent biodegradability of carbohydrates provides them with some environmental advantages as well.

In addition to cellulose, a very abundant material in wood is lignin, a complex binding material that serves to hold wood together. Lignin is a biopolymer containing groups such as those shown in Figure 20.2. Unlike carbohydrate cellulose, which has a uniform structure and is composed entirely of glucose monomer units, lignin

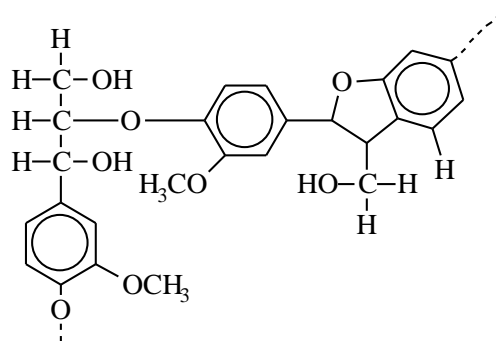
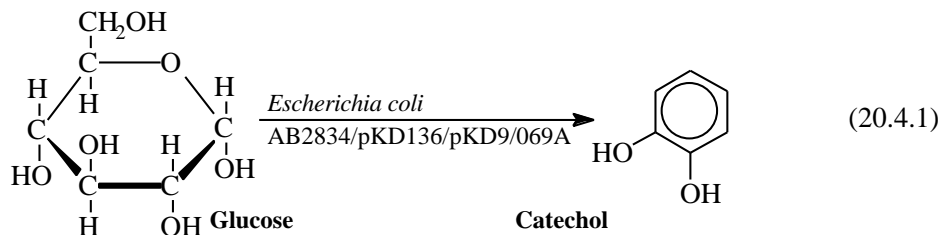


Figure 20.2 Segment of lignin polymer.

has a variable structure. This is a severe detriment to its use as a chemical feedstock. One of the more promising potential uses for abundant lignin resources is the production of phenolic compounds. A major detriment to the use of lignin in green chemistry is its resistance to any sort of biological processes that might be considered for its conversion to useful products.

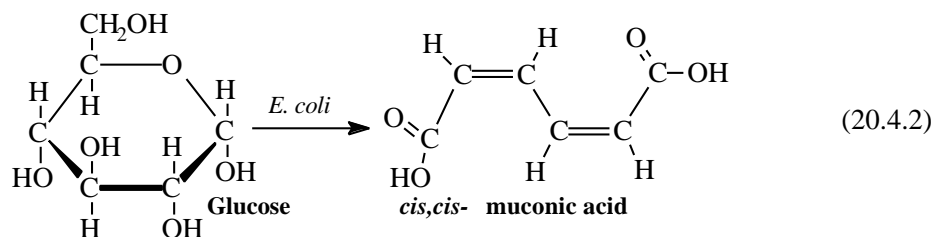
A potentially important chemical reagent that can be synthesized from glucose by biological means is catechol. Catechol is used to make a wide range of pharmaceutical chemicals, pesticides, antioxidants, and other chemical feedstocks. The

standard synthesis of catechol involves using petroleum-derived benzene and propylene to make cumene, elimination of acetone from cumene by treatment with oxygen to give phenol, then oxidation of phenol to catechol with 70% hydrogen peroxide. These steps require some rather severe conditions, involve toxic benzene feedstock and toxic phenol intermediate, and require stringent precautions in handling highly reactive hydrogen peroxide. Through elegant genetic manipulation, *E. coli* AB2834/pKD136/pKD9/069A, a strain of *Escherichia coli* bacteria, has been developed that catalyzes the following overall biotransformation:

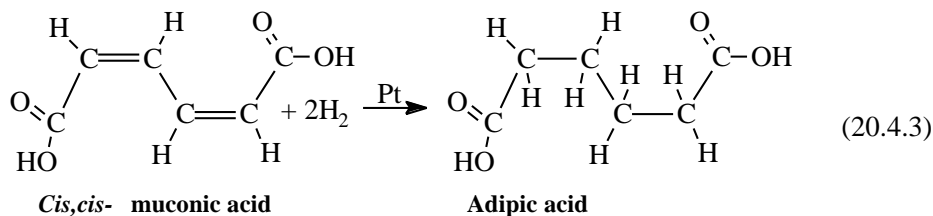


A variation of the biosynthesis described above can be used to make adipic acid, a key feedstock in the manufacture of nylon 6,6. As with catechol, the conventional chemical synthesis of adipic acid commonly starts with benzene, which is hydrogenated to cyclohexane. Air oxidation of cyclohexane over metal catalysts yields cyclohexanol and byproduct cyclohexanone. The oxidation of cyclohexanol with 60% nitric acid yields adipic acid. Elevated temperature (250°C), high pressure (50 atm), and the use of strong oxidant nitric acid, which carries with it the possibility of nitrogen oxides release, are problems with the synthesis.

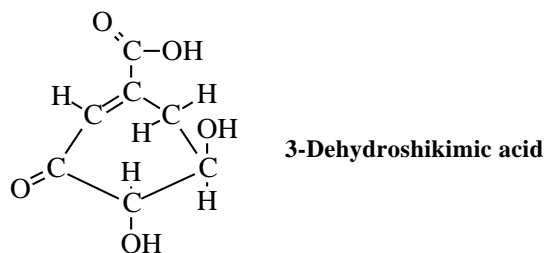
As an alternative biological synthesis of adipic acid, a microbial process that uses a genetically engineered strain of bacteria given the designation *Escherichia coli* AB2834/pKD136/pKD8.243A, was developed capable of converting glucose to *cis-cis*-muconic acid by way of a catechol intermediate



Hydrogenation at a pressure of only 3 atm over a platinum catalyst can then be used to convert the *cis,cis*-muconic acid to adipic acid:

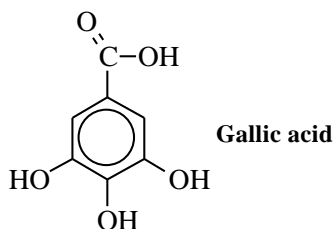


3-Dehydroshikimic acid is a substance that can now be made by environmentally benign biological synthesis. This substance has the potential to substitute for substances made by less environmentally friendly means as a feedstock and as an antioxidant. As shown by its formula,



3-dehydroshikimic acid is a hydroaromatic compound. It is an intermediate in the biosynthesis of aromatic amino acids, adipic acid, catechol, gallic acid, and vanillin. This compound has been synthesized biologically in significant yields with genetically modified *Escherichia coli* strain KL3 using as a feedstock glucose as well as a mixture of D-glucose, D-xylose and L-arabinose.⁵ This suggests the possibility of biosynthesis of 3-dehydroshikimic acid as a raw material for the manufacture of other organic compounds.

The facile biosynthesis of 3-dehydroshikimic acid and its ability to act as an antioxidant suggest that it may become an important antioxidant. Such antioxidants are added to foods, oils, fats, fuels and lubricants to prevent their being oxidized by reacting with oxygen and reactive intermediates in the oxidation process. At present, the most commonly used antioxidants are butylated hydroxytoluene, synthesized from petroleum feedstocks, and propyl gallate made from gallic acid,



which is derived from natural source gall nuts or tara powder.

20.5 REAGENTS

Judicious selection of **reagents** and **media** for carrying out chemical processes can be a crucial factor in developing a successful green chemistry process. Use of a benign feedstock may be of relatively little use if large quantities of hazardous reagents are required for its processing. Media, which frequently consist of solvents, are discussed in more detail in Section 20.6.

Two important factors driving reagent selection are **product selectivity** and **product yield**. High-product selectivity means higher conversion of raw material to the desired product. High-product yield means a high percentage of the desired product is obtained relative to the maximum yield calculated from stoichiometric considerations. Both high-product selectivity and high-product yield reduce the amounts of extraneous material that must be handled and separated.

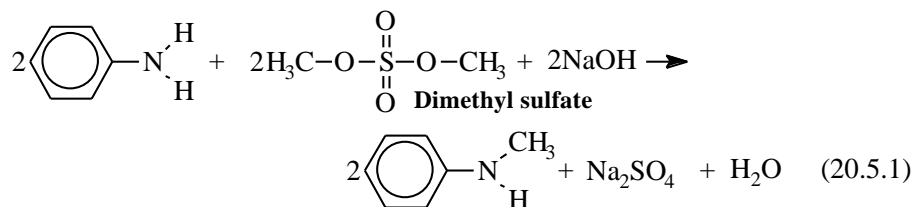
In selecting safe media and feedstocks, consideration of structure-activity relationships can be very useful. It is known that certain structures or functional groups tend to create particular kinds of hazards. For example, the presence of oxygen and nitrogen—particularly multiple nitrogen atoms—in proximity in a molecule tends to make it reactive or even explosive. The presence of the N–N=O functional group results in **N-nitroso** compounds (**nitrosamines**), many of which are carcinogenic. The presence of chemical structures that can result in donation of methyl groups to biomolecules may make a compound mutagenic or carcinogenic; substitution of longer-chain hydrocarbon groups can reduce this hazard.

In evaluating the safety of reagents and choosing safer alternatives, special attention should be given to **functional groups** consisting of particular groupings of atoms. The carcinogenic potential of the N–N=O group was mentioned above. Aldehydes tend to be irritants to animals and are photochemically active, so that they can contribute to smog formation when released to the atmosphere. Whenever possible it is best to use alternative compounds when particular functional groups are likely to be a problem. It is also sometimes possible to mask functional groups to produce less dangerous forms, then unmask them at the point in the synthesis where the functionality is needed.

Oxidation is one of the most common operations in chemical synthesis. The nature of oxidation often requires harsh conditions and harsh reagents, such as permanganate (MnO_4^-), chromium(VI) compounds (such as potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$), toxic and costly osmium tetroxide, or *m*-chloroperbenzoic acid. Therefore, one of the main objectives of green chemistry has been the development of more benign oxidizing agents and oxidation reactions.

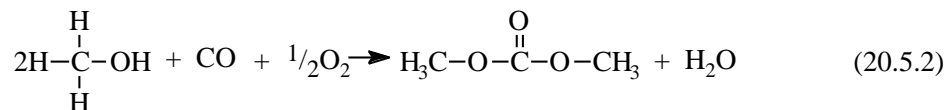
Reduction is a common operation in chemical synthesis. As with oxidation, the reagents used for reduction tend to be reactive and difficult to handle. Two of the most common such reagents are lithium aluminum hydride and tributyltin hydride. LiAlH_4 is rather hazardous to use. Tributyltin hydride can release volatile tin-containing products that pose toxicity hazards. Both oxidizing and reducing agents used in chemical synthesis produce byproducts that must be carefully disposed of at significant expense.

Alkylation consists of the attachment of alkyl groups, such as the methyl group, $-\text{CH}_3$, to an organic molecule. The attachment of an alkyl group to a nitrogen in an amine is used as a step in the synthesis of a variety of dyes, pharmaceuticals, pesticides, plant growth regulators, and other specialty chemicals. In such cases, alkylation is commonly carried out using alkyl halides or alkyl sulfates in the presence of a base as shown below for the attachment of a methyl group to N in aniline:

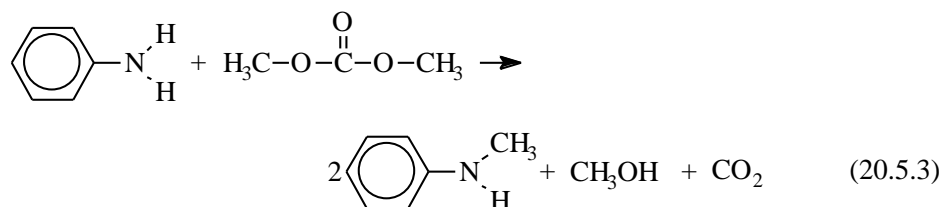


This kind of reaction produces significant amounts of inorganic salt byproduct, such as Na_2SO_4 . also, alkyl halides and alkyl sulfates pose toxicity concerns; dimethyl sulfate is a primary carcinogen, causing cancer without the need for bioactivation.

Relatively nontoxic dialkyl carbonates are very effective alkylating agents that promise to provide a safer alternative to alkyl halides or sulfates for some kinds of alkylation reactions.⁶ The promise of dimethyl carbonate for methylation (alkylation in which the methyl group, -CH₃, is attached) has been enhanced by the straightforward synthesis of this compound from methanol and carbon monoxide in the presence of a copper salt:

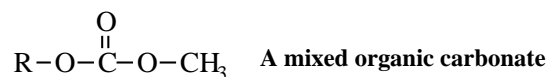


Dimethyl carbonate can be used for methylation of nitrogen in amine compounds at a temperature of 180°C under continuous-flow gas-liquid phase-transfer catalysis conditions (which involve transfer of organic ionic reactant species between water and an organic phase) as shown below for the methylation of aniline:



The use of dimethyl carbonate as a methylating agent offers the twin advantages of up to 99% efficiency of conversion to product with selectivities of 99% or more for the monomethyl product. The byproducts are innocuous carbon dioxide and methanol, which can be recirculated through the process for making dimethyl carbonate (Reaction 20.5.2). Dimethyl carbonate is useful, for example, in making monomethyl organonitrogen derivatives required for the synthesis of analgesics, such as Ibuprofen.

Mixed organic carbonates in which a methyl group is attached to the carbonate as is a much larger organic moiety, R,



can be very effective methylating agents, as examples, giving anisoles from phenols, and N-methyl aniline from aniline.⁷ A major advantage is that the high-molar-mass mixed organic carbonates are much higher boiling than dimethylcarbonate and reactions using them can be run at ambient pressure rather than in pressurized reaction vessels.

20.6 MEDIA

Media is a term used to refer to the matrix in which or on which chemical processes occur. The type and strength of interaction between the media and reactants in a chemical process play a very important role in determining the type, degree, and rate of the process. Although media may include solids upon which reactions take place, by far the most common type of media consists of liquid

solvents in which reagents are dissolved. Solvents interact to various extents and in various ways with the solutes dissolved in them. An important phenomenon is **solvation**, in which the solvent molecules interact with solute molecules. A common example of this is the attraction of polar water solvent molecules for dissolved cations and anions as shown in Chapter 7, [Figure 7.3](#). This ability makes water an extraordinarily good solvent for ionic substances—acids, bases, and salts—that are commonly used in chemical reactions. The ability of water to form hydrogen bonds is particularly important in its ability to dissolve a wide range of biological materials capable of forming hydrogen bonds.

By their nature, solvents cause more environmental and health problems than do other participants in the chemical synthesis process. Most solvents are volatile and tend to escape into the workplace and atmosphere. Hydrocarbon solvents are flammable and can cause explosive mixtures with air. Released to the atmosphere, they can be instrumental in causing formation of photochemical smog (see Chapter 16). A number of adverse health effects are attributed to solvents. Carbon tetrachloride, CCl_4 , causes lipid peroxidation in the body and can cause severe damage to the liver. Benzene causes blood disorders and is suspected of causing leukemia. Volatile C_5 - C_7 alkanes damage nerves and can result in a condition known as peripheral neuropathy. The possibility of causing cancer is always a consideration in dealing with solvents in the workplace.

20.7 THE SPECIAL IMPORTANCE OF SOLVENTS

As noted in the preceding section, solvents are a uniquely important type of media in which chemical processes are carried out. Beyond their uses as reaction media, solvents have other uses, particularly in separation, purification, and cleaning. Water is the most abundant and safest solvent and should be used wherever possible. In fact, one of the main objectives of the practice of green chemistry is to convert processes to the use of water solvent wherever possible. However, water is not a suitable solvent for a wide range of organic substances used industrially. Therefore, the use of organic solvents consisting of hydrocarbons and hydrocarbon derivatives, such as chlorinated hydrocarbons, is unavoidable in many cases. In addition to serving as reaction media, organic solvents are used as cleaners, degreasers, and as extractants to remove organic substances from solids. A major use of organic solvents is as the liquid **vehicle** to enable the application, spreading, and impregnation (such as of cloth) of dissolved or suspended dyes and other agents in formulations of paints, coatings, inks, and related materials.

A key consideration in selecting and using a solvent for the proper practice of green chemistry consists of its toxicological and environmental effects on biological systems. This obviously includes toxic effects to humans. Physical properties, such as volatility, density, and solubility, are important in estimating potential environmental and biological effects. Lipophilicity, the tendency to dissolve lipid tissue, is a measure of the ability of a solvent to penetrate skin and hence is an important factor in determining its biological effects. The environmental persistence and biodegradation of solvents should be considered. Special care must be taken to not use or at least prevent the release to the atmosphere of volatile solvents that may become involved in photochemical reactions leading to photochemical smog

formation. The formerly widespread use of volatile chlorofluorocarbon solvents as blowing agents to produce porous plastics and plastic foams resulted in widespread dissipation of these ozone destroying chlorofluorocarbon vapors to the atmosphere (see Chapter 16, Section 16.4).

Much of the progress that has been made toward the goal of green chemistry has come with replacement of potentially troublesome solvents with less dangerous ones. Some pertinent examples of such replacement are shown in Table 20.1. The best solvent to use, when possible, is water. It is discussed below.

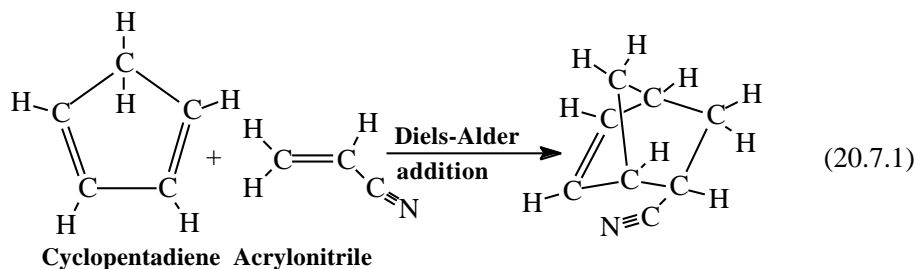
Water, the Greenest Solvent

Although it does not truly dissolve hydrophobic organic substances, but may hold them in suspension as finely divided colloidal matter, water can often be used in place of organic solvents as a medium for organic reactions and for other applications. In addition to its not dissolving organic substances, water suffers from the disadvantage of reacting strongly with some reagents, such as AlCl_3 used in Friedel-Crafts reactions, strongly reducing LiAlH_4 , and metallic sodium used in some applications. On the other hand, precisely because water is such a poor solvent for organic substances—the **hydrophobic effect**—some organic reactions proceed better in a water medium. Water is an excellent solvent for some of the more hydrophilic biological molecules, such as glucose, that are gaining favor as reactants for green chemical processes.

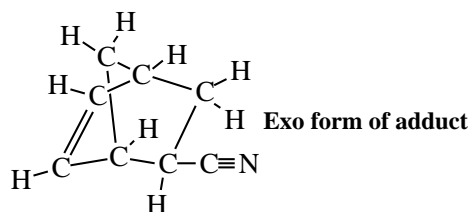
Table 20.1 Solvents for Which Substitutes Have Been Developed

Solvent	Disadvantages of solvent	Substitute	Characteristics of substitute
Benzene	Toxic, causing blood disorders and suspected of causing leukemia, metabolized to toxic phenol	Toluene	Much less toxic than benzene because of the presence of a metabolically oxidizable methyl substituent group; produces hippuric acid metabolite
<i>n</i> -Hexane	Neurotoxic causing peripheral neuropathy manifested by mobility loss, reduced sensations in extremities	2,5-Dimethylhexane	Lacks toxicity characteristics of <i>n</i> -hexane, significantly higher boiling point may be a disadvantage
Glycol ethers	Ethylene glycol monomethyl ether and ethylene glycol monoethyl ether have adverse reproductive and developmental effects in animals	1-Methoxy-2-propanol	Less toxic than the glycol ethers, but still effective as a solvent
Various organic solvents	Flammability, toxicity, poor biodegradability, tendency to contribute to photochemical smog	Supercritical fluid carbon dioxide	Widely available, good solvent for organic solutes, readily removed by evaporation, non-polluting, except as a greenhouse gas if allowed to escape

An interesting reaction attributed to the hydrophobic effect is illustrated by the following Diels-Alder addition reaction carried out with the poorly water-soluble reactants held as a suspension in water:⁸



It is believed that the reaction actually occurs in water, and the water-insoluble product comes out of the water as an organic phase. A significant aspect of the reaction is that the Diels-Alder addition product is in the endo form as opposed to the exo form shown below:



The preferential formation of the endo form is attributed to so-called better hydrophobic packing and consequent less exposure to solvent water for the transition state leading to the endo form. In general, for reactions of the type described above, the reactants existing separately in water have a higher energy than they would in the more “friendly” surroundings of an organic solvent. The transition state between two hydrophobic reactants in water has less exposure to the “hostile” water environment than do the two reactants separately. This energetically favored transition state leads to a more facile reaction in water and favors products in which exposure to water is minimized.

In cases where the hydrophobic effect of water as described above is excessive, it is possible to reduce it by adding organic cosolvents. One solvent that is useful for this purpose is ethanol. Ethanol has the additional advantage of being readily prepared from biological sources and being degradable. Therefore, it, too, largely meets the criteria of a “green” solvent.

Largely ignored during the development of organic synthesis, water is getting renewed attention as a medium for organic chemical reactions and processes. This is due largely to water’s being the ultimate green solvent with no detrimental environmental, safety (flammability), or toxicological aspects to its use. As the price for feedstocks for making organic solvents has increased—an especially painful phenomenon with rising petroleum prices in year 2000—the fact that water is essentially free increases its attractiveness. Water is a good solvent for many biological materials gaining favor as green chemistry reagents, and, as discussed above, its repulsion of some organophilic reagents can be advantageous in some

cases. Water-insoluble organic products are readily separated from water without having to distill off an organic solvent. The control of heat and temperature is an important aspect of many chemical processes. For heat and temperature control, water is the best solvent to use because of its very high heat capacity (see Chapter 11, Table 11.1).

Dense Phase Carbon Dioxide as a Solvent

Substances that are normally considered to be gases take on special properties when highly compressed. The general diagram shown in Figure 20.3 shows that, at temperatures exceeding a critical temperature, T_c , and pressures exceeding a critical pressure, P_c , the distinction between liquid and gas disappears and a substance becomes a **supercritical fluid**. The most widely studied supercritical fluid is that formed by carbon dioxide, for which T_c is 31.1°C and P_c is 73.8 atm. Supercritical fluids have many useful solvent properties. It has also been found, however, that highly compressed carbon dioxide below the critical point, where it is not supercritical, but may exist as a mixture of liquid and gas, has some excellent solvent properties as well. The term **dense phase fluid** is used to designate a highly compressed, dense substance that may be a supercritical fluid, highly compressed gas, or mixture of gas and liquid.⁹

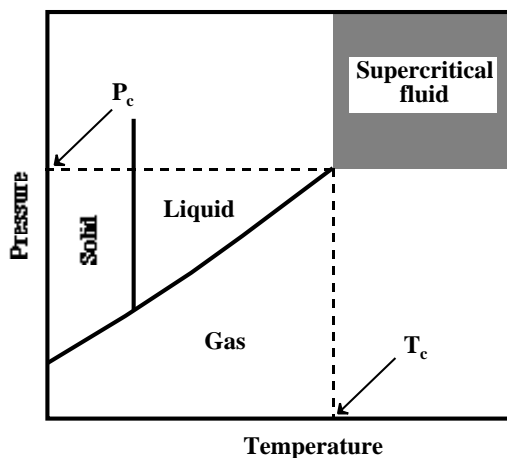


Figure 20.3 Temperature-pressure plot showing supercriticality.

Dense phase fluids have a number of interesting solvent properties and have been extensively investigated as extractants and for chromatographic separations (supercritical fluid chromatography). An important characteristic of these fluids is their much lower viscosities than conventional liquids; that of supercritical CO_2 is only about 1/30 the viscosity of liquids normally used as solvents. This means that solutes diffuse much more readily in supercritical fluids, thus enabling them to react much faster. The wide latitude within which pressures and temperatures of dense phase fluids may be changed enables their properties to be varied widely.

Supercritical fluid carbon dioxide is an excellent solvent for organic solutes. This has led to its uses in place of organochlorine solvents for cleaning metal parts and in dry cleaning. A major advantage of supercritical fluid carbon dioxide in some

applications is that it is readily evaporated from solutes by releasing pressure. This has led to interest in the solvent as a vehicle for paints and coatings. With the appropriate apparatus, the released carbon dioxide can be reclaimed and recompressed back to a supercritical state for recycling. This capability tends to overcome criticism of the use of carbon dioxide, which is, of course, a greenhouse gas when released to the atmosphere. Supercritical fluid carbon dioxide has a highly organophilic nature, which may be excessive for some applications with more polar or ionic solutes. Addition of polar cosolvents, such as methyl alcohol, can overcome this disadvantage. A further advantage of supercritical fluid carbon dioxide as a solvent is its ability to dissolve gases, enhanced by the very high pressure under which supercritical fluid carbon dioxide must be maintained. This enables reactions to occur efficiently with gaseous reactants in supercritical fluid carbon dioxide that would otherwise not be possible.

Supercritical fluids have some disadvantages. The major disadvantage of such solvents is the special apparatus required to maintain supercritical conditions. However, supercritical fluid carbon dioxide's advantages of low cost, high abundance from a number of sources, nontoxic nature, nonflammability, and the fact that it is not classified as a volatile organic solvent (VOC) will undoubtedly lead to increased uses of this solvent in the future.

20.8 SYNTHETIC AND PROCESSING PATHWAYS

From the standpoint of green chemistry, the ideal chemical synthesis begins with a readily available, inexpensive, nontoxic material and converts it by one step with 100% yield and 100% atom efficiency to the desired product. Although such a totally efficient synthesis almost never can be realized, it does provide a framework within which to attempt to produce the desired product using the least possible reagent and reaction media (solvent) by the most straightforward possible pathway. When this is done, pollution is minimized at its source and the objectives of the practice of green chemistry are fulfilled.

In evaluating the degree to which synthetic and processing pathways are consistent with the practice of green chemistry, it is useful to consider three major categories of synthetic reactions, recognizing that two or even all three may be involved in making a desired product:

- **Addition reactions** in which all reagents are incorporated into product
- **Substitution reactions** in which a reagent or parts of it replace groups on another reagent
- **Elimination reactions** in which substances are eliminated from the feedstock as byproducts

Where they can be used, addition reactions are best because all starting materials end up in product, and there is no byproduct for which disposal or finding another use is required. By their nature, substitution reactions generate at least some byproducts. Elimination reactions do not require input of materials other than feedstocks, but do generate byproducts requiring disposal or recycling.

20.9 THE ROLE OF CATALYSTS

In some cases, catalysts tend to add to the hazards of chemical processes and to produce troublesome byproducts and product contaminants. This can occur, for example, with homogeneous catalysts that are intimately mixed with the reagents involved in chemical synthesis. Catalysts that are most amenable to the practice of green chemistry are heterogeneous catalysts, such as molecular sieves, that can be kept entirely separate from products. Insofar as possible, such catalysts should be nontoxic.

Although they do not involve catalysts in the strictest sense, alternatives to chemical or heat energy for the introduction of energy required to carry out a chemical process can produce a much more environmentally attractive process. The two main ways of doing this are through the use of electricity or of photochemical energy.

The passage of a direct current of electricity through a reaction medium can cause both reductions and oxidations to occur. Reduction, the addition of electrons, e^- , can occur at the relatively negatively charged cathode, and oxidation, the loss of electrons, at the relatively positively charged anode. A simple example of an electrochemical process used to manufacture industrial chemicals occurs when a direct current is passed through molten sodium chloride, NaCl. At the cathode, sodium ion is reduced,



and at the anode, chloride ion is oxidized to elemental chlorine gas,



giving the following net reaction:



The reaction utilizes electrical energy efficiently and occurs with 100% atom economy.

Electrochemical oxidation and reduction can be controlled by the potentials applied, by the media in which they occur, and by the electrodes used. In a sense, electrochemical processes use “matter-free” reagents; no other approach comes any closer to the attainment of ideal green chemistry.

Enzymatically catalyzed reactions carried out by genetically engineered microorganisms can be combined with electrochemical processes to give very clean and efficient syntheses in some cases. An example of such a synthesis is that of corduritol C, for which the reaction scheme is shown in [Figure 20.4](#).¹⁰ In this case, the starting material shown by the first structure in [Figure 20.4](#) was made enzymatically by the action of *Escherichia coli* pDTG601 bacteria. The rest of the reaction scheme consists of electrochemical reactions and hydrolysis reactions.

Photochemical reactions use the energy of photons of light or ultraviolet radiation to cause reactions to occur. For electromagnetic radiation of frequency ν , the energy of a photon is given by the equation $E = h\nu$, where h is Planck's constant.

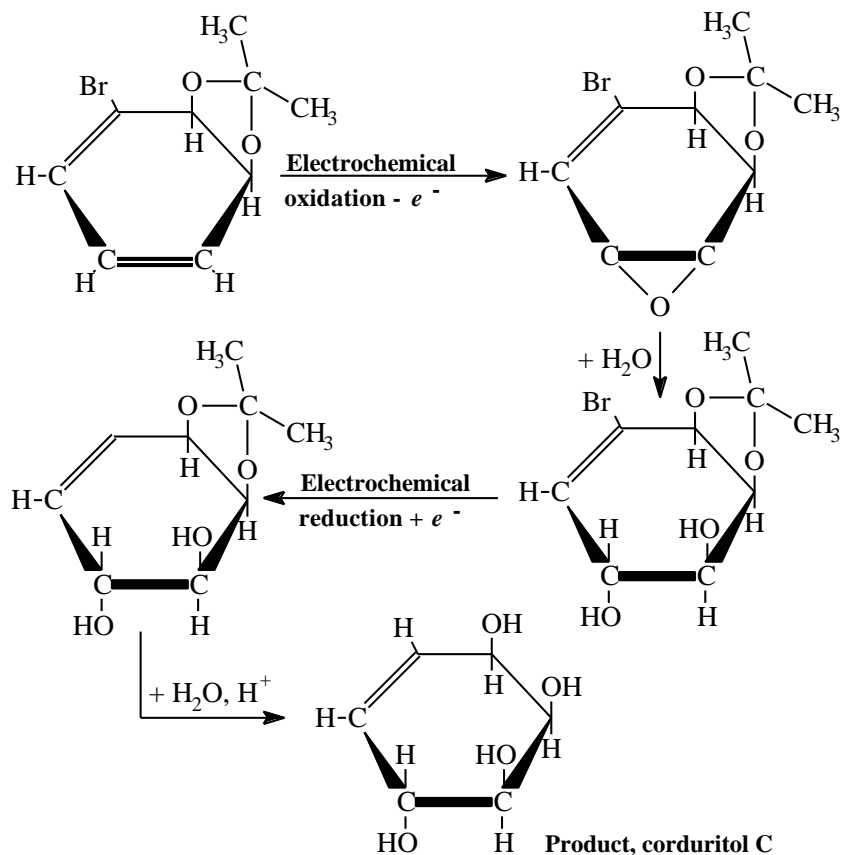
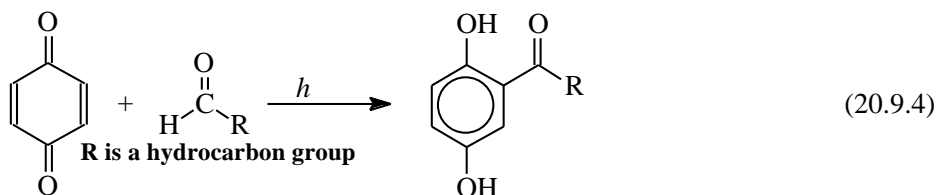


Figure 20.4 Use of electrochemical processes in the synthesis of corduritol C.

There is a significant potential to use photochemical energy to cause synthesis reactions to occur more efficiently and with less production of waste byproducts than nonphotochemical processes.¹¹ One example is the acylation of benzoquinone with an aldehyde to produce an acylhydroquinone, an intermediate used to make some specialty polymers:



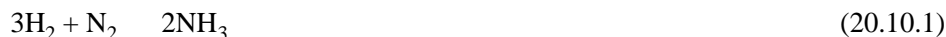
This reaction occurs with 100 % atom economy. Unlike the standard Friedel-Crafts type of reaction, which utilize the catalytic effect of Lewis acid-type acidic halides, particularly aluminum chloride, AlCl_3 , the photochemical process does not require moisture- and air-sensitive, potentially reactive catalytic substances.

20.10 BIOLOGICAL ALTERNATIVES

Organically bound carbon is the basic building block of the world's vast organic chemical and polymer industries. At the present time, virtually all of this carbon is provided by petroleum and natural gas. Although these sources are vast and can supply needed carbon for many decades, particularly if alternatives to their use for fuel are developed, they are depletable resources and ultimately nonsustainable. A renewable, sustainable alternative is provided by photosynthetically produced biomass. Biomass consists largely of biopolymeric cellulose, hemicellulose, starch, lignin, and protein, all with the potential to be used directly or after chemical or biochemical modification. In addition, biological processes produce a variety of monomers, including sugars (glucose, sucrose), oils and fats (triglycerides), waxes, amino acids, and substances extractable from plants, such as hydrocarbon terpenes. It has been estimated that biological sources of these materials could supply essentially all U. S., and presumably world, needs for fixed carbon chemical feedstocks.¹² Much of the research effort at the U.S. National Renewable Energy Laboratory in Golden, Colorado is devoted to the development of cost-effective practical methodologies for the selective conversion of biological polymers and monomers to useful chemicals and chemical feedstocks.

Biological waste materials constitute much of the solid waste for which disposal is required. One attractive alternative is the use of much of this solid waste as a raw material, or food source, in the biological synthesis of desired chemical feedstocks.

An attractive feature of biological systems is the enzyme-mediated reactions that they carry out under very mild ambient conditions. The industrial Haber process for the synthesis of ammonia from elemental hydrogen and nitrogen,



is carried out over a catalyst under extreme conditions of 500°C temperature and 200 atmospheres (atm) pressure. Bacteria, such as the nitrogen-fixing *Rhizobium* bacteria on the roots of leguminous plants use enzymes to fix atmospheric nitrogen at soil temperatures of 25°C or less and atmospheric pressure.

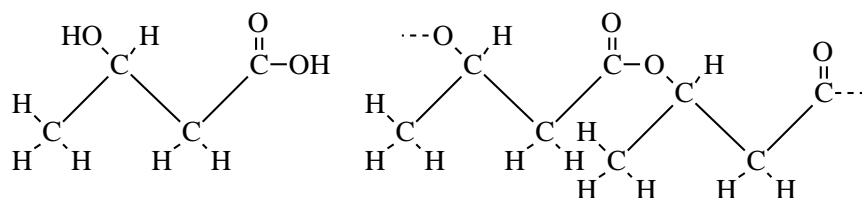
In industrial chemical processes, oxidation is frequently carried out by a variety of oxidants using a wide range of catalysts. Many of the oxidants, such as dichromate or ozone, as well as many of the catalysts, pose hazards of high reactivity and toxicity. Natural systems, in contrast, carry out all the oxidations required by using molecular oxygen, O₂, and hydrogen peroxide, H₂O₂. In so doing, organisms use elegant reaction schemes employing enzymes as catalysts. These enzymes include mono-oxygenases to catalyze oxidation by O₂ and peroxidases to catalyze oxidations with hydrogen peroxide.

Biopolymers

The manufacture of synthetic polymers consumes large quantities of petroleum for raw material, and synthetic and natural polymers make up a large fraction of solid waste. For these reasons, it is desirable to both make polymers from renewable biological sources and to synthesize and use polymers that will biodegrade after disposal. Nature has provided a large variety of polymer factories, producing useful

polymers such as cellulose in wood and cotton, lignin in wood, and protein in wool and silk. With the exception of degradation-resistant lignin, these polymers, made by organisms, are also degradable by organisms, particularly fungi and bacteria. Synthetic polymers can be tailored for biodegradability. One approach that has been tried widely is to synthesize biodegradable polymers with modified starch. Other possibilities for the preparation of biodegradable polymers is to synthesize them from biodegradable monomers, including polylactic acid, polyvinyl alcohol, polyesters, cellulose acetate, and poly{3-hydroxybutyrate-3-hydroxyvalerate}.

Aside from the natural polymers that have long been known and used, such as cotton, the most active current area of research in natural polymers involves the poly(hydroxyalkanoate) esters (alkanoates). These polymers were found to be produced by fluorescent *Pseudomonads* and other bacteria,¹³ which generate and store them as reserves of carbon and energy. Their production has now been achieved in transgenic (genetically engineered) plants.¹⁴ The first of the biologically produced poly(hydroxyalkanoate) esters to be identified was a polymer of 3-hydroxybutyric acid (Figure 20.5). Numerous other hydroxyacids synthesized by microorganisms can be used to make these esters. It is possible to make poly(hydroxyalkanoate) ester polymers ranging in properties from flexible, stretchable elastomers and rubbery polymers to stiff, brittle solid plastics. In addition to their being biosynthesized without the need of petroleum-based monomers, the alkanoates reflect their biological origins in being completely biodegradable.



3-Hydroxybutyric acid Repeating unit of poly(3-hydroxybutyrate) polymer

Figure 20.5 A common hydroxy acid monomer, 3-hydroxybutyric acid, and representation of a polymer formed from this class of compound.

Clearly, the alkanoate ester polymers are “green” chemicals, and there is a great deal of interest in using them as commercial polymers. Although these polymers have been made on a small industrial scale by bacterial fermentation using plant-derived glucose as a substrate, this pathway may be too costly for commercial production. Production by plants is an attractive alternative, and some success has been achieved in so doing with plants genetically engineered with bacterial genes for alkanoate ester production. Genes from the bacterium *Alcaligenes eutrophus* have been added to *Arabidopsis thaliana*, to produce a genetically engineered plant that subsequently produced up to 14% dry mass of poly(hydroxybutyric acid) in its leaves. Alkanoate polymers and copolymers with varying chain lengths—hence, variable properties—have now been produced by plants. For example, genetically engineered *Arabidopsis* and *Brassica* have been shown to generate a copolyester of 3-hydroxybutyrate and 3-hydroxyvalerate.

A potential concern with the hydroxybutyrates has to do with the use of one member of the series as an illicit drug. So-called gamma-butyrate, 4-hydroxybutyric acid, is the infamous “date-rape” drug, which has caused fatalities to victims who have ingested it with “spiked” drinks.

20.11 APPLICATIONS OF GREEN CHEMISTRY

The principles of green chemistry are being more widely applied in industry to reduce emissions and save money and materials. Significant success in this area has been achieved at Dow Chemical’s manufacturing complex in Midland, Michigan.¹⁵ This vast operation makes more than 500 products, including polymers, packaging, pesticides, and drugs. Although a strong effort had been made to reduce emissions for many years, in the mid-to-late-1990s a program was undertaken to further reduce production and emission of undesirable byproducts.

As is normally the case with efforts of this kind, substantial waste reductions were achieved by simple measures. One of these was the reduction by 15,500 kg/year of organochlorine compound emissions from the manufacture of Saran plastic by transferring product to a storage tank twice a day instead of only once. When only one transfer per day was performed, the tank was filled to capacity with liquid and vaporized organochlorine compound emissions had to be vented to waste. Retaining these materials for recycle from the half-filled tanks saved the company an estimated \$34,000 per year.

The production of formaldehyde-containing tar wastes from resin manufacture was curtailed by switching catalysts and making processing changes. The cost of making these changes was \$330,000, but they are estimated to save the company \$3.3 million each year in waste-treatment costs. Improved recovery of unreacted reagent in the production of 2,4-D herbicide resulted in a 66% reduction in tetrachloroethylene wastes. Previous procedures in the manufacture of SB latex binder in paint were carried out so that wastes that required incineration because of hazardous impurities were mixed with recyclable wastes, thus requiring that the whole mixture be incinerated. Changing that practice to keep the recyclable wastes segregated enabled a higher degree of recycling, reducing butadiene and styrene wastes by 35%. A problem with butadiene used to make resins and rubber is that it forms butadiene dimer during storage. Butadiene dimer is an unusable material that requires disposal. Formation and deposition of the dimer in apparatus tends to clog equipment. Refrigeration of butadiene from the supplier was found to lower the rate of dimer formation and to significantly reduce wastes requiring disposal from this source. Reduction of wastes and pollutants released was achieved in the manufacture of Ethocel, a product with diverse applications as a stabilizing agent and binder in foods, drugs, and other materials. Use of a steam system to purge volatile substances from the product along with a refrigerated condenser to the system used to recover volatile substances reduced both wastes and pollutants released in the form of chloroethane and toluene by between 50 % and 60 %.

The success of Dow’s “green chemistry” initiative at Midland, though modest in terms of cost savings relative to the annual budget of the complex, has provided impetus for additional initiatives of a similar nature in the company. Similar measures are planned for the company’s large petrochemical manufacturing operation in Freeport, Texas. In addition, the company has set a goal of reducing toxic chemicals

emissions by 50 to 90 % over the decade ending in 2005. Similar initiatives are ongoing, with other companies raising the prospect of much lower chemical emissions in the future.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Laws that have emphasized dealing with environmental problems after they have occurred represent a ¹ _____ approach. Green chemistry can be defined as ² _____

_____.

Green chemistry is ³ _____ because it is less costly, makes efficient use of raw materials, and does not cause an intolerable accumulation of hazardous-waste products. Two often complementary approaches to the practice of green chemistry are ⁴ _____

_____.

The equation

$$\frac{\text{Molecular mass of desired product}}{\text{Total molecular mass of materials generated}}$$

defines ⁵ _____. The ultimate in the parameter just defined is achieved when ⁶ _____. The practice of avoiding use or production of flammable, reactive, explosive, or toxic substances occurs under the category of ⁷ _____. Some attributes of a feedstock consistent with the practice of green chemistry are ⁸ _____

_____.

In a generalized sense, the overall process of obtaining a useful product from a feedstock, such as petroleum or biological materials, may be divided into the three categories of ⁹ _____

_____.

Biopolymers from plants that have the potential for use as biological feedstocks include ¹⁰ _____.

In some cases, an advantage of biological feedstocks is their high ¹¹ _____ content. In some cases, a disadvantage of biological feedstocks is the ¹² _____ of biomolecules. Probably the most important biological raw materials for chemical synthesis are ¹³ _____ produced by plants, ¹⁴ _____.

_____.

In addition to cellulose, a very abundant material in wood is ¹⁵ _____. A feedstock used to make a wide range of pharmaceutical chemicals, pesticides, antioxidants, and other chemical feedstocks

that can now be synthesized biologically from glucose is ¹⁶ _____. Another feedstock used to make nylon 6,6 that potentially can be synthesized biologically is ¹⁷ _____. Two important factors driving reagent selection are ¹⁸ _____. The fact that certain structures or functional groups tend to create particular kinds of hazards is taken into account by considering ¹⁹ _____. In evaluating the safety of reagents and choosing safer alternatives, special attention should be given to ²⁰ _____ consisting of particular groupings of atoms. A process in chemical synthesis that uses reagents such as permanganate (MnO_4^-), chromium(VI) compounds, osmium tetroxide, or *m*-chloroperbenzoic is ²¹ _____, whereas a process using LiAlH_4 is ²² _____. Attachment of a methyl group in chemical synthesis is part of the more general process of ²³ _____. A safer substitute for dimethyl sulfate in methylation reactions is ²⁴ _____. The byproducts of this methylation reagent are ²⁵ _____. The matrix in which or on which chemical processes occur is referred to as ²⁶ _____ of which the most common type consists of ²⁷ _____. The interaction of solvent molecules with solute molecules is referred to as ²⁸ _____. A solvent that causes lipid peroxidation in the body is ²⁹ _____ whereas volatile $\text{C}_5\text{-C}_7$ can cause ³⁰ _____. A solvent used to enable application of dissolved or suspended dyes and other agents in formulations of paints, coatings, inks, and related materials is known as a ³¹ _____. A solvent used as a substitute for toxic benzene is ³² _____. The "greenest solvent" is ³³ _____. An effect of water solvent that occurs by repulsion of reactants or intermediates by water is the ³⁴ _____. The control of heat and temperature in chemical reactions is aided in water because of water's ³⁵ _____. Carbon dioxide at a temperature above its critical temperature and a pressure above its critical pressure is a ³⁶ _____. An important characteristic of dense phase fluids, including supercritical fluids is their very low ³⁷ _____ compared with normal liquids. A major advantage of supercritical fluid carbon dioxide in some applications is that it is ³⁸ _____ by releasing pressure. The major disadvantage of supercritical fluid solvents is ³⁹ _____. Three major categories of synthetic reactions are ⁴⁰ _____ of which the best type from the standpoint of green chemistry is ⁴¹ _____. Catalysts that are most amenable to the practice of green chemistry are ⁴² _____ because they ⁴³ _____. Two alternatives to heat for introducing energy into a reaction scheme are ⁴⁴ _____. The passage of a direct current of electricity through a reaction medium can cause both ⁴⁵ _____ to occur. The three factors by which electrochemical oxidation and reduction can be controlled are ⁴⁶ _____. Photochemical reactions use the energy of ⁴⁷ _____ to cause reactions to occur. An attractive feature of biological systems for performing chemical process is that enzyme-mediated reactions occur under ⁴⁸ _____.

_____ conditions. Natural systems carry out all the oxidations required by using relatively benign ⁴⁹ _____. Aside from the natural polymers, such as cellulose in cotton, that have been long known and used, the most active current area of research in natural polymers involves the ⁵⁰ _____. The first of these to be identified were polymers of ⁵¹ _____.

Answers to Chapter Summary

1. command and control
2. the sustainable exercise of chemical science and technology within the framework of good practice of industrial ecology such that the use and handling of hazardous substances are minimized and such substances are never released to the environment
3. sustainable
4. use existing chemicals, but make them by environmentally benign syntheses and substitute chemicals made by environmentally benign syntheses for existing chemicals
5. atom economy
6. there is no byproduct
7. hazard reduction
8. place minimal demands on Earth's resources, safe as possible, acquisition and refining should be safe, and renewable.
9. source identification and acquisition, separation of desired components from source, and conversion of isolated feedstock to desired product
10. cellulose, hemicellulose, starch, lignin, and proteins
11. oxygen
12. complexity
13. carbohydrates
14. including glucose, fructose, sucrose, and starch
15. lignin
16. catechol
17. adipic acid
18. product selectivity and product yield
19. structure-activity relationships
20. functional groups
21. oxidation
22. reduction
23. alkylation
24. dimethyl carbonate
25. carbon dioxide and methanol
26. media
27. solvents
28. solvation
29. carbon tetrachloride
30. peripheral neuropathy
31. vehicle

32. toluene
33. water
34. hydrophobic effect
35. very high heat capacity
36. supercritical fluid
37. viscosities
38. readily evaporated from solutes
39. the special apparatus required to maintain supercritical conditions
40. addition reactions, substitution reactions, and elimination reactions
41. addition reactions
42. heterogeneous catalysts
43. can be kept entirely separate from products
44. electrical energy and photochemical energy
45. reductions and oxidations
46. by the potentials applied, by the media in which they occur, and by the electrodes used
47. photons of light or ultraviolet radiation
48. very mild ambient
49. molecular oxygen and hydrogen peroxide
50. poly(hydroxyalkanoate) esters (alkanoates)
51. 3-hydroxybutyric acid

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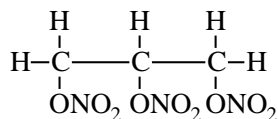
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QUESTIONS AND PROBLEMS

1. What are four categories of hazardous substances based on chemical properties? Which important class of hazardous substances does this classification scheme omit?
2. What is the practice of relating chemical formulas to toxicity?
3. What are three major categories of hazardous substances that are candidates for reduction in the practice of green chemistry?
4. Compare the preparation of a polymeric plastic or rubber from petroleum feedstock with the production of poly(hydroxyalkanoate) ester polymers from biological sources in terms of the three major steps in obtaining a feedstock and converting it to a useful product shown in [Figure 20.1](#).

5. Although abundant, why is lignin not a good candidate as a raw material?
6. In addition to its uses as a feedstock, what is a potential application of 3-dehydroshikimic acid?
7. Compare the roles of product selectivity and product yield in reagent selectivity for green chemistry.
8. What structural features of the compound,



would make it hazardous? What is the nature of the hazard?

9. What is the potential use of dialkyl carbonates, such as dimethyl carbonate, in green chemical synthesis?
10. Calculate the atom economy of Reaction 20.5.3.
11. What are some uses of organic solvents other than for reaction media? What are some of the drawbacks of organic solvents for these uses?
12. In terms of interaction with reagents, what is the greatest disadvantage of water as a solvent? What is the greatest advantage of water as a solvent for a variety of solutes of biological origin?
13. What is a dense phase fluid? What form of dense phase carbon dioxide is produced at very high pressures and slightly elevated temperature?
14. How can water's hydrophobic effect be reduced? What is a "green" substance commonly used in lowering the hydrophobic effect?
15. What are the advantages of supercritical fluid carbon dioxide solvent? Why is carbon dioxide's volatility an advantage in some cases?
16. Why are polar cosolvents added to supercritical fluid carbon dioxide? What is a common polar cosolvent?
17. What are three major categories of synthetic reactions? Which of these is the most consistent with the practice of green chemistry? Why?
18. Discuss how electrons and photons can be regarded as catalysts. In what respects are they "massless" reagents?
19. Discuss and compare the conditions and relative advantages and disadvantages of the Haber process and its biological alternatives.
20. What are two major related advantages of biopolymers in the practice of green chemistry? What are some of the most common biopolymers?
21. What is a common type of biopolymer synthesized by some kinds of bacteria and now by genetically engineered plants?

22. List some of the applications of green chemistry that have actually been applied on an industrial scale.
23. Suggest how refrigeration of apparatus and storage tanks can aid green chemistry in industry. Are there any potential disadvantages to refrigeration?
24. What is the relationship of industrial ecology to green chemistry? In which ways are industrial ecology and green chemistry complementary?
25. What is the meaning of “command and control?” What are its limitations in the control of pollution?
26. In what sense does the practice of green chemistry ensure environmental quality by “natural,” self-regulating means?
27. What is the role of sustainability in the practice of green chemistry?
28. How is atom economy defined? In what sense is it a key aspect of the practice of green chemistry?