Academic Award

Professor Michael J. Krische
University of Texas at Austin

Hydrogen-Mediated Carbon—Carbon Bond Formation

Innovation and Benefits

A fundamental aspect of chemistry involves creating chemical bonds between carbon atoms. Chemical processes commonly used to make such bonds usually also generate significant amounts of waste. Professor Krische developed a broad new class of chemical reactions that make bonds between carbon atoms using hydrogen and metal catalysts. This new class of reactions can be used to convert simple chemicals into complex substances, such as pharmaceuticals, pesticides, and other important chemicals, with minimal waste.

Reductions mediated by hydrogen, termed "hydrogenations", rank among the most widely used catalytic methods employed industrially. They are generally used to form carbon–hydrogen (C–H) bonds. Professor Michael J. Krische and his coworkers at the University of Texas at Austin have developed a new class of hydrogenation reactions that form carbon–carbon (C–C) bonds. In these metal-catalyzed reactions, two or more organic molecules combine with hydrogen gas to create a single, more complex product. Because all atoms present in the starting building-block molecules appear in the final product, Professor Krische's reactions do not generate any byproducts or wastes. Hence, Professor Krische's C–C bond-forming hydrogenations eliminate pollution at its source.

Prior to Professor Krische's work, hydrogen-mediated C–C bond formations were limited almost exclusively to the use of carbon monoxide in reactions such as alkene hydroformylation (1938) and the Fischer-Tropsch reaction (1923). These prototypical hydrogen-mediated C–C bond formations are practiced industrially on an enormous scale. Yet, despite the importance of these reactions, no one had engaged in systematic research to develop related C–C bond-forming hydrogenations. Only a small fraction of hydrogenation's potential as a method of C–C coupling had been realized, and the field lay fallow for nearly 70 years.

Professor Krische's hydrogen-mediated couplings circumvent the use of preformed organometallic reagents, such as Grignard and Gilman reagents, in carbonyl and imine addition reactions. Such organometallic reagents are highly reactive, typically moisture-sensitive, and sometimes pyrophoric, meaning that they combust when exposed to air. Professor Krische's coupling reactions take advantage of catalysts that avoid the hazards of traditional organometallic reagents. Further, using chiral hydrogenation catalysts, Professor Krische's couplings generate C–C bonds in a highly enantioselective fashion.

Catalytic hydrogenation has been known for over a century and has stood the test of time due its efficiency, atom economy, and cost-effectiveness. By exploiting hydrogenation as a method of C–C bond formation, Professor Krische has added a broad, new dimension to one of chemistry's most fundamental catalytic processes. The C–C bond-forming hydrogenations developed by Professor Krische allow chemists to create complex organic molecules in a highly selective fashion, eliminating both hazardous starting materials and hazardous waste. Commercial application of this technology may eliminate vast quantities of hazardous chemicals. The resulting increases in plant and worker safety may enable industry to perform chemical transformations that were too dangerous using traditional reagents.

Small Business Award

NovaSterilis Inc.

Environmentally Benign Medical Sterilization Using Supercritical Carbon Dioxide

Innovation and Benefits

Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilization techniques use ethylene oxide or gamma radiation, which are toxic or have safety problems. NovaSterilis invented a technology that uses carbon dioxide and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor gamma radiation.

None of the common methods for medical sterilization is well-suited to sterilizing delicate biological materials. The sterility of these materials is critical. Distribution of contaminated donor tissues by tissue banks has resulted in serious infections and illnesses in transplant patients. The two most widely used sterilants (ethylene oxide and gamma radiation) also raise toxicity and safety concerns. Ethylene oxide is a mutagenic, carcinogenic, volatile, flammable, reactive gas. Residues of ethylene oxide remain in the sterilized material, increasing the risk of toxic side effects. Gamma radiation is highly penetrating and is lethal to all cells. Neither ethylene oxide nor gamma radiation can sterilize packaged biological products without eroding their physical integrity.

NovaSterilis, a privately held biotechnology company in Ithaca, NY, has successfully developed and commercialized a highly effective and environmentally benign technique for sterilizing delicate biological materials using supercritical carbon dioxide (CO_2). NovaSterilis licensed a patent for bacterial inactivation in biodegradable polymers that was issued to Professor Robert S. Langer and his team at the Massachusetts Institute of Technology. NovaSterilis then enhanced, expanded, and optimized the technology to kill bacterial endospores. Their supercritical CO_2 technology uses low temperature and cycles of moderate pressure along with a peroxide (peracetic acid) and small amounts of water. Their Nova 2200™ sterilizer consistently achieves rapid (less than one hour) and total inactivation of a wide range of microbes, including bacterial endospores. The mechanism of bacterial inactivation is not well-understood, but does not appear to involve bacterial cell lysis or wholesale degradation of bacterial proteins.

The new technology is compatible with sensitive biological materials and is effective for a wide range of important biomedical materials including: (a) musculoskeletal allograft tissue (e.g., human bone, tendons, dermis, and heart valves) for transplantation; (b) biodegradable polymers and related materials used in medical devices, instruments, and drugs; (c) drug delivery systems; and (d) whole-cell vaccines that retain high antigenicity. Besides being a green chemical technology, supercritical CO_2 sterilization achieves "terminal" sterilization, that is, sterilization of the final packaged product. Terminal sterilization provides greater assurance of sterility than traditional methods of aseptic processing. Sterilization of double-bagged tissue allows tissue banks to ship terminally sterilized musculoskeletal tissues in packages that can be opened in operating rooms by surgical teams immediately prior to use. NovaSterilis's patented technology addresses the market need in tissue banks as well as other needs in the biomedical, biologics, medical device, pharmaceutical, and vaccine industries. By the end of 2006, NovaSterilis had sold several units to tissue banks.

Greener Synthetic Pathways Award

Professor Kaichang Li, Oregon State University; Columbia Forest Products; Hercules Incorporated

Development and Commercial Application of Environmentally Friendly Adhesives for Wood Composites

Innovation and Benefits

Adhesives used in manufacturing plywood and other wood composites often contain formaldehyde, which is toxic. Professor Kaichang Li of Oregon State University, Columbia Forest Products, and Hercules Incorporated developed an alternate adhesive made from soy flour. Their environmentally friendly adhesive is stronger than and cost-competitive with conventional adhesives. During 2006, Columbia used the new, soy-based adhesive to replace more than 47 million pounds of conventional formaldehyde-based adhesives.

Since the 1940s, the wood composites industry has been using synthetic adhesive resins to bind wood pieces into composites, such as plywood, particleboard, and fiberboard. The industry has been the predominate user of formaldehyde-based adhesives such as phenol–formaldehyde and urea–formaldehyde (UF) resins. Formaldehyde is a probable human carcinogen. The manufacture and use of wood composite panels bonded with formaldehyde-based resins release formaldehyde into the air, creating hazards for both workers and consumers.

Inspired by the superior properties of the protein that mussels use to adhere to rocks, Professor Li and his group at Oregon State University invented environmentally friendly wood adhesives based on abundant, renewable soy flour. Professor Li modified some of the amino acids in soy protein to resemble those of mussels' adhesive protein. Hercules Incorporated provided a critical curing agent and the expertise to apply it to commercial production of plywood.

Oregon State University, Columbia Forest Products (CFP), and Hercules have jointly commercialized soy-based adhesives to produce cost-competitive plywood and particleboard for interior uses. The soy-based adhesives do not contain formaldehyde or use formaldehyde as a raw material. They are environmentally friendly, cost-competitive with the UF resin in plywood, and superior to the UF resin in strength and water resistance. All CFP plywood plants now use soy-based adhesives, replacing more than 47 million pounds of the toxic UF resin in 2006 and reducing the emission of hazardous air pollutants (HAPs) from each CFP plant by 50 to 90 percent. This new CFP plywood is sold under the PureBond™ name. During 2007, CFP will replace UF at its particleboard plant; the company is also seeking arrangements with other manufacturers to further the adoption of this technology.

With this technology, those who make and use furniture, kitchen cabinetry, and other wood composite materials have a high-performing formaldehyde-free alternative. As a result, indoor air quality in homes and offices could improve significantly. This technology represents the first cost-competitive, environmentally friendly adhesive that can replace the toxic UF resin. The technology can greatly enhance the global competitiveness of U.S. wood composite companies. In addition, by creating a new market for soy flour, currently in over-supply, this technology provides economic benefits for soybean farmers.

Greener Reaction Conditions Award

Headwaters Technology Innovation

Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

Innovation and Benefits

Hydrogen peroxide is an environmentally friendly alternative to chlorine and chlorine-containing bleaches and oxidants. It is expensive, however, and its current manufacturing process involves the use of hazardous chemicals. Headwaters Technology Innovation (HTI) developed an advanced metal catalyst that makes hydrogen peroxide directly from hydrogen and oxygen, eliminates the use of hazardous chemicals, and produces water as the only byproduct. HTI has demonstrated their new technology and is partnering with Degussa AG to build plants to produce hydrogen peroxide.

Hydrogen peroxide (H_2O_2) is a clean, versatile, environmentally friendly oxidant that can substitute for environmentally harmful chlorinated oxidants in many manufacturing operations. However, the existing manufacturing process for H_2O_2 is complex, expensive, and energy-intensive. This process requires an anthraquinone working solution containing several toxic chemicals. The solution is reduced by hydrogen in the presence of a catalyst, forming anthrahydroquinone, which then reacts with oxygen to release H_2O_2. The H_2O_2 is removed from the solution with an energy-intensive stripping column and then concentrated by vacuum distillation. The bulk of the working solution is recycled, but the process generates a waste stream of undesirable quinone-derived byproducts that requires environmentally acceptable disposal.

Headwaters Technology Innovation (HTI) has produced a robust catalyst technology that enables the synthesis of H_2O_2 directly from hydrogen and oxygen. This breakthrough technology, called NxCat™, is a palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable byproducts. It produces H_2O_2 more efficiently, cutting both energy use and costs. It uses innocuous, renewable feedstocks and generates no toxic waste.

NxCat™ catalysts work because of their precisely controlled surface morphology. HTI has engineered a set of molecular templates and substrates that maintain control of the catalyst's crystal structure, particle size, composition, dispersion, and stability. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for H_2O_2 up to 100 percent.

The NxCat™ technology enables a simple, commercially viable H_2O_2 manufacturing process. In partnership with Degussa AG (a major H_2O_2 manufacturer), HTI successfully demonstrated the NxCat™ technology and, in 2006, completed construction of a demonstration plant. This demonstration plant will allow the partners to collect the data necessary to design a full-scale plant and begin commercial production in 2009. The NxCat™ process has the potential to cut the cost of H_2O_2 significantly, generating a more competitively priced supply of H_2O_2 and increasing its market acceptance as an industrial oxidant. Except for its historically higher price, H_2O_2 is an excellent substitute for the more frequently used—and far more deleterious—chlorinated oxidants. The NxCat™ technology has the benefit of producing an effective, environmentally preferable oxidant (H_2O_2) without the waste or high cost associated with the traditional process.

Designing Greener Chemicals Award

Cargill, Incorporated

BiOH™ Polyols

Innovation and Benefits

Foam cushioning used in furniture or bedding is made from polyurethane, a man-made material. One of the two chemical building blocks used to make polyurethane is a “polyol.” Polyols are conventionally manufactured from petroleum products. Cargill’s BiOH™ polyols are manufactured from renewable, biological sources such as vegetable oils. Foams made with BiOH™ polyols are comparable to foams made from conventional polyols. As a result, each million pounds of BiOH™ polyols saves nearly 700,000 pounds of crude oil. In addition, Cargill’s process reduces total energy use by 23 percent and carbon dioxide emissions by 36 percent.

Polyols are key ingredients in flexible polyurethane foams, which are used in furniture and bedding. Historically, polyurethane has been made from petrochemical polyols. The idea of replacing these polyols with biobased polyols is not new, but the poor performance, color, quality, consistency, and odor of previous biobased polyols restricted them to limited markets. Previous biobased polyols also suffer from poor chemical reactivity, resulting in foam with inferior properties.

Cargill has successfully developed biobased polyols for several polyurethane applications, including flexible foams, which are the most technically challenging. Cargill makes BiOH™ polyols by converting the carbon–carbon double bonds in unsaturated vegetable oils to epoxide derivatives and then further converting these derivatives to polyols using mild temperature and ambient pressure. BiOH™ polyols provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams. These foams set a new standard for consistent quality with low odor and color. Foams containing BiOH™ polyols retain their white color longer without ultraviolet stabilizers. They also are superior to foams containing only petroleum-based polyols in standard tests. In large slabstock foams, such as those used in furniture and bedding, BiOH 5000 polyol provides a wide processing window, improved comfort factor, and reduced variations in density and load-bearing capacity. In molded foams such as automotive seating and headrests, BiOH 2100 polyol can enhance load-bearing or hardness properties relative to conventional polyols.

Use of BiOH™ polyols reduces the environmental footprint relative to today's conventional polyols for polyurethane production. BiOH™ polyols "harvest" carbon that plants remove from the air during photosynthesis. All of the carbon in BiOH™ polyols is recently fixed. In conventional polyols, the carbon is petroleum-based. Replacing petroleum-based polyols with BiOH™ polyols cuts total energy use by 23 percent including a 61 percent reduction in nonrenewable energy use, leading to a 36 percent reduction in carbon dioxide emissions. For each million pounds of BiOH™ polyol used in place of petroleum-based polyols, about 700,000 pounds (2,200 barrels) of crude oil are saved, thereby reducing the dependence on petroleum. BiOH™ polyols diversify the industry's supply options and help mitigate the effects of uncertainty and volatility of petroleum supply and pricing. Cargill is the first company to commercialize biobased polyols on a large scale in the flexible foam market. Formulators can now use biobased polyols in flexible foam without compromising product performance. That the top North American polyol users choose BiOH™ polyols is validation of Cargill's accomplishment.