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Abstract: Chlorine-based solvents have a terrible public image as ozone eaters. Under the Montreal Protocol, many chlorine-containing compounds, including several dry-cleaning agents, are banned internationally. Now fluorine, which sits just above chlorine in the Periodic Table, may be set to redeem the family name. Researchers are analyzing the potential for fluorine-based chemicals to speed up important industrial reactions, conserve catalysts and solvents, and use less energy in the process. Fluorine's rise as a green chemical began a decade ago in the Corporate Research Laboratories of Exxon Research and Engineering Co. István T. Horváth and colleagues were searching for a better way to oxidize methane to methanol, a major feedstock for the production of fuels and chemicals. They never found it, but in the course of their work they hit on something potentially much more useful. They began to investigate using fluorine-containing solvents instead of familiar organic solvents such as aliphatic hydrocarbons, ethers, and amines. Their experiments showed that these previously little-investigated "fluorous" solvents simply would not mix with the conventional solvents in their reactions.

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Green Chemistry

Shy Chemicals Offer a Solution

Sporting fluorine atoms where standard organic compounds have hydrogen, new touch-me-not solvents and catalysts bid to help industrial chemistry clean up its act

Chlorine-based solvents have a terrible public image as ozone eaters. Under the Montreal Protocol, many chlorine-containing compounds, including several dry-cleaning agents, are banned internationally. Now fluorine, which sits just above chlorine in the Periodic Table, may be set to redeem the family name.

Researchers are touting the potential for fluorine-based chemicals to speed up important industrial reactions, conserve catalysts and solvents, and use less energy in the process. "The unique properties of fluorine atoms ... offer unparalleled opportunities for chemists to speed up and clean up their acts," says Dennis Curran of the University of Pittsburgh.

Fluorine's rise as a green chemical began a decade ago in the Corporate Research Laboratories of Exxon Research and Engineering Co. István T. Horváth (now at Eötvös Loránd University in Budapest, Hungary) and colleagues were searching for a better way to oxidize methane to methanol, a major feedstock for the production of fuels and chemicals. They never found it, but in the course of their work they hit on something potentially much more useful. Trying to improve on the widely used industrial process for converting alkenes into useful materials, they began to investigate using fluorine-containing solvents instead of familiar organic solvents such as aliphatic hydrocarbons, ethers, and amines. Their experiments showed that these previously little-investigated "fluorous" solvents simply would not mix with the conventional solvents in their reactions.

The new fluorous solvents sport C-F bonds where standard solvents have C-H or C-Cl bonds. Like their forebears, they readily dissolve small molecules such as carbon monoxide and hydrogen. But in other ways they are dramatically different. For one thing, fluorine's high electronegativity, or affinity for electrons, makes them reluctant to mix with conventional solvents at room temperature. "They are like liquid Teflon: Organic and inorganic things don't stick," says Curran, an early fluorous-chemistry enthusiast.

That chemical standoffishness, Horváth realized, might help chemists solve some longstanding problems. At the top of the list is catalysis. Chemists use two main kinds of catalysts: homogeneous ones, which begin their reactions dissolved in the same solution as the starting materials, and heterogeneous ones, which are bound to solid particles that mingle with the dissolved reactants but remain separate from them. Homogeneous catalysts tend to be highly efficient, but reclaiming them from solution once the reaction is complete often requires environmentally noxious solvents that increase the overall costs of the process. Heterogeneous catalysts, by contrast, can be easily separated from the product, cleaned up, and reused. But they are also less efficient, and the high temperatures and pressures often needed to make them practical add costs and environmental burdens of their own.

Fluorous catalysts offered a third path. These catalysts have sprouted a fluorous appendage, so they readily dissolve in fluorous solvents. Poured into a solution of conventional reactants, such a fluorous phase remains separate, like oil on water, at room temperature. When warmed, though, the two liquids mingle, bringing the dissolved fluorous catalyst into direct contact with the starting materials, where they can react very effectively. As the mixture cools, the phases separate again. Nonfluorous reaction products remain with the nonfluorous organic phase, so they can easily be tapped off and the catalyst phase recycled (see figure).

"During reaction, you have homogeneous catalysis. During separation, it's heterogeneous. It's like having your cake and eating it too," Curran says. Curran is hoping to cash in on that potential: He has created a spin-off company, Fluorous Technologies Inc., that now supplies a growing market for fluorous reagents.

Other researchers who have taken the ball and run with it include John Gladysz, one of Horváth's early collaborators. Now at the University of Erlangen-Nürnberg, Germany, Gladysz and colleagues have extended fluorous chemistry to workhorses of the chemical industry such as metal-catalyzed hydrogenations, hydrosilylations, and hydroborations — atom-swapping reactions used to produce everything from agrochemicals to pharmaceuticals.

Gladysz says his team aims to create a "parallel universe" of fluorous chemicals that would react like traditional reagents and catalysts — phosphines, aliphatic amines, pyridines, arenes, and sulfur compounds — but that would readily dissolve in fluorous solvents. Already the group has developed a fluorous version of aryl iodide, an oxidizing agent used throughout the chemical industry. Normally, chemists discard the byproducts of aryl iodide, but the fluorous versions of the chemicals can be recycled.

Labs around the world are spinning variations on the fluorine theme. Jean-Pierre Bégué, Danièle Bonnet-Delpon, and colleagues at the French national research agency CNRS in Châtenay-Malabry have developed several new fluorinated compounds in which fluorine replaces only about half of the hydrogen atoms in conventional organic compounds. Bégué says they have found that when they use partially fluorinated alcohols such as hexafluoroisopropanol in synthesizing organic compounds, the oxidation reactions are faster, cleaner, and easier to control. What's more, the only byproduct is water, making the reactions even more environmentally friendly. The team hopes to create fluorous counterparts for processes that now rely heavily on toxic, ozone-eating chlorinated solvents.

Other groups are ringing changes on the number of phases. In recent experiments, Curran and collaborators in Osaka, Japan, led by Ilhyong Ryu of Osaka Prefecture University in Sakai have sandwiched a fluorous solvent between two otherwise miscible organic solvents — one heavier and one lighter than the fluorous phase. Different starting materials dissolved in each organic phase diffuse across the fluorous phase and react on the other side. Using such three-phase systems, the team has carried out a pair of common processes, the bromination of alkenes and the dealkylation of aromatic ethers by boron tribromide.

This "liquid membrane" approach, Curran says, provides an easy way to keep heat-generating reactions under control. Instead of using energy-consuming cooling systems or machines that slow the mixing of the reaction ingredients, chemical engineers can control reaction rates simply by changing the thickness of the fluorous barrier. And because the fluorous reaction components simply have to pass through the fluorous solvent, not dissolve in it as they do in a two-phase system, the chemicals can get by with many fewer fluorine atoms, Curran says. That should make them less damaging should any escape into the environment. Curran sees applications for such reactions in many areas, including the preparation of handed forms of drug molecules.

Gladysz's team, meanwhile, hopes to eradicate fluorous solvents from fluorous reactions altogether. Building on earlier work by Curran, the researchers have found that many fluorous catalysts work just as well in conventional solvents and can still be recycled as readily. The key to the technique is that many perfluorinated catalysts become markedly more soluble in conventional solvents as the temperature rises. The chemists warm the vessel containing the reagents, feed in the catalyst, and then cool the system after the reaction finishes. As the catalyst becomes less soluble, it drops out of solution to be filtered off. Gladysz and his team are also working to create reactions with fluorous catalysts bound to Teflon shavings, which can simply be filtered off at the end of the process.

Fluorous chemistry is not a panacea for the chemical industry. Many reaction systems are still off-limits to the approach because no one has made the necessary fluorous reagents or catalysts. Horváth says that problem will solve itself as more researchers start working in the area. Environmental concerns could also cloud the field's future. Although fluorous compounds are safer than their chlorine-based counterparts, they could still cause problems, and many chemists worry that chemically stable, environmentally persistent fluorous solvents could lead to a buildup of troublesome greenhouse gases. But Curran says careful handling and the design of nonvolatile fluorous reagents can minimize those risks. If so, environmentally benign chemical processes could shift from their present patchwork of niches into the industrial mainstream. Fluorine could be green, after all.

PHOTO (COLOR): Escape artist. Dennis Curran and other aficionados hope to harness fluorine-rich chemicals' quirky unmixing ability.

PHOTO (COLOR): Mix masters. Fluorous solvents can make catalysts and reaction products easy to retrieve.

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By David Bradley, Writer in Cambridge, U.K.
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