MEETING BRIEFS

Near the Lights of Vegas, Chemists Are on a Roll

LAS VEGAS—Some 9000 researchers gathered here last month for the 214th national meeting of the American Chemical Society (ACS). As temperatures outside topped 100, hot topics in the meeting included a machine capable of tracking the chemistry of particles in the atmosphere in real time and polymers that break down into drug molecules.

Probing Particles on the Fly

Measured by weight, particles and dust are just a tiny part of the atmosphere. Measured by influence, they are a major constituent. Particles ranging from dust and soot to ice and sea salt affect everything from urban smog and global warming to the Antarctic ozone hole. But cumbersome, slow instruments have kept researchers from studying the size and makeup of individual particles drifting on the wind. Instead they have had to collect them, take them back to the laboratory, and analyze them en masse.

K. PRATHER/UC RIVERSIDE

Taking the air. A portable laser-based particle analyzer.

At the meeting, a team led by Kimberly Prather at the University of California, Riverside, showed off an instrument that should let researchers get acquainted with particles one by one, in real time. At about the size of a steamer trunk, her team's laser-based mass spectrometer is small enough to be taken into the field. There the device can suck in particles and measure their sizes and compositions on the fly.

The Riverside instrument, a similar portable device recently developed by Daniel Murphy and his colleagues at the National Oceanic and Atmospheric Administration in Boulder, and others in the works are a "major advance," says Margaret Tolbert, an atmospheric chemist at the University of Colorado, Boulder. "They will revolutionize the way we look at single particles in the atmosphere." Indeed, Prather and her colleagues have already shown off their device by tracking how the chemistry of sea-salt particles changed as they blew from the coast of southern California some 70 kilometers inland to the town of Riverside—the first time researchers have been able to track such a change in real time.

It was researchers studying the Antarctic ozone hole in the 1980s who first began to realize that particles can essentially act as catalysts for atmospheric chemistry, providing a surface that favors a host of reactions that do not take place readily in the gas phase. Today, ice particles in stratospheric clouds are widely considered a key culprit in the chain of events causing the ozone hole, fostering reactions yielding a highly reactive form of chlorine that breaks down ozone. Atmospheric researchers are now also struggling to understand how the chemistry and size of sulfate particles from pollution influence their ability to cool the planet.

To study these types of particles, researchers typically take sampling equipment up in aircraft, filter out particles from the air stream, and then examine them on the ground using high-power electron microscopes and x-ray detectors. But this can take a long time, during which particles collected on filters can react with one another, skewing the results. Such factors encourage researchers simply to determine the average sizes and compositions of large numbers of particles.

To get a closer look at individual particles, Prather and her colleagues built a specialized version of a time-of-flight mass spectrometer (TOFMS), a device that determines the composition of a sample by ionizing its chemical components and gauging the atomic and molecular weight of the ions. Lab-based TOFMSs normally detect either negative or positive ions, but not both. To get an accurate picture of atmospheric particles with a single machine, the team had to develop a version that could do both sets of ions at once, says Prather. Because different kinds of particles, such as sulfates or sea salt, can usually be recognized by their characteristic size range, Prather's team built in a size analyzer as well.

The machine works by first sucking particles from the outside air into a tube. The particles are then blasted through a nozzle and down a tube at supersonic speeds into a vacuum. Before they reach the full vacuum, friction causes different-sized particles to slow down, with smaller particles affected slightly less than larger ones. Once inside the vacuum, the particles don't change speed. They fly through two laser beams 6 centimeters apart, which clock their speeds, from which the device calculates the particles' sizes.

In a chamber at the bottom of the vacuum tube, the machine fires a third laser pulse to blow each particle apart and turn its components into positively and negatively charged ions. A gradient of electrical charge created by a series of electrode plates then pushes negative ions in one direction and positive ions in the other, toward a pair of ion detectors on either side of the chamber. Lighter ions reach the detectors faster than heavier ones do, so the machine can determine each ion's atomic or molecular weight—and hence its chemical makeup—by recording its time of flight.

After constructing two of the portable instruments and calibrating them with a third lab-based machine, Prather and her colleagues used them at three different ground-based sites to track how the chemistry of sea-salt particles changed as they passed over polluted southern California. Changes in the measured molecular weights showed that particles that begin their lives over the ocean primarily as sodium chloride end up reacting with nitric acid in the atmosphere to produce sodium nitrate particles. "The results clearly show that as the peaks at 81 and 83 [sodium chloride] disappear, the 108 peak [sodium nitrate] grows in," says Prather.

"This is likely the first time [gas-particle chemistry] has been monitored directly in the atmosphere in real time," she adds. With efforts already under way with these instruments to gauge the chemistry of different sulfate particles that may play a key role in moderating global warming, it certainly won't be the last.

Polymer Painkiller

Polymers—the stuff of plastics—may soon be serving as drugs. These long, chainlike molecules are already familiar in medicine, for example, in implants and in the biodegradable capsules that ferry drugs into the intestines. In a new strategy reported at the ACS meeting, however, a team of researchers from Rutgers University in Piscataway, New Jersey, has developed a polymer that breaks down into a drug—in this case a relative of aspirin.

The new polymer painkiller has yet to be tested in animals or humans. But the researchers think it may offer a welcome treatment for inflammatory bowel disease, which requires long-term administration of anti-inflammatory drugs delivered only to the intestine. The polymer should bypass the acidic environment of the mouth and stomach, then break down to form the drug under the alkaline conditions found in the intestine. "It's a very innovative approach," says chemical engineer Nicholas Peppas of Purdue University in West Lafayette, Indiana, who himself works in the field of biodegradable polymers and drug delivery. "It would be a very important development if it works."

The Rutgers team did not set out to make a polymeric painkiller at all, says its leader, chemist Kathryn Uhrich. Rather, they were working to alter a class of polymers to make it easier for the body to degrade them. The polymers they were using, known as polyanhydrides, already have a variety of medical uses, such as in biodegradable sutures. But certain bonds in the chemical "linking groups" between the polymer's individual units—or monomers—don't break down readily. To make the polymer suitable for use as a temporary scaffold for tissue regeneration and wound healing, Uhrich and her colleagues decided to replace one kind of linking group, known as ethers, with esters, which have bonds that break more readily.

Uhrich then recognized, she says, that the modified polymer itself "breaks down into something that is useful": salicylic acid, the same anti-inflammatory compound that results from the metabolism of aspirin. The breakdown also releases sebacic acid, an inert byproduct of other biodegradable polymers that have been approved by the Food and Drug Administration, says Uhrich.

When the polymer is swallowed, the breakdown should be delayed because the bonds that link the monomers are very stable under acidic conditions. When Uhrich and her colleagues tested their polymers in an acidic bath with a pH of 5—about the acidity of the mouth and stomach—they found little change. But when they raised the pH to 9, equivalent to what is found in the intestine, the polymers began to degrade, releasing first a burst of salicylic acid monomers, and then a steady stream of them.

That behavior could give the polymer drug an edge over current treatments for inflammatory bowel disease. The most popular drug, sulfasalazine, breaks down in the intestine to release salicylic acid. But sulfasalazine also releases unwanted byproducts that can trigger skin rashes, headaches, and other problems. New formulations that have recently come on the market encase salicylic acid in polymers that degrade in the intestine. But the degradation does not always occur in the right place, says Kiron Das, chief of gastroenterology at the University of Medicine and Dentistry of New Jersey in New Brunswick. Uhrich and her colleagues should get an inkling of whether their polymer painkiller can do any better later this year, when they plan to begin testing it in animals.

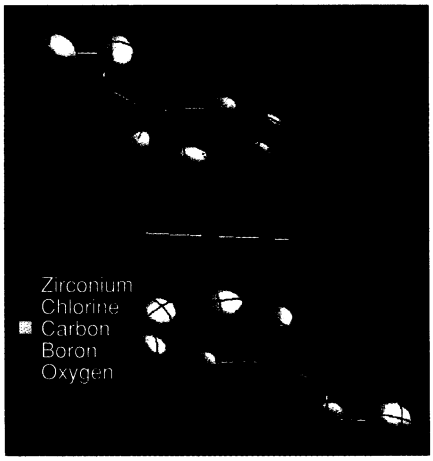
–**Robert F. Service**

INDUSTRIAL CHEMISTRY

Olefin Catalyst Keeps Things Short

A new catalyst can be as big a boon for a chemical company as a blockbuster drug is for a pharmaceutical manufacturer. That is because catalysts are the key to many industrial processes, such as creating plastics and other materials. These matchmaker molecules, for example, can coax tens of thousands of identical chemical groups to link together into the polymer chains that are the basis of plastics. Now, a team of chemists from the University of Rochester in New York has created a catalyst with a new talent: keeping those chains short.

Reported in this week's issue of the *Journal of the American Chemical Society*, the new molecule belongs to a class of catalysts known as metallocenes, which have swept through the polymer industry in recent years because of their unmatched ability to form long chains without unwanted byproducts. The new catalyst creates ultrashort polymers called α-olefins, just a few units long, which serve as a feedstock for making everything from soaps and detergents to garbage bags. But like its fellow metallocenes, the boron- and zirconium-containing molecule does its job without creating unwanted byproducts, promising a jump in efficiency over conventional α-olefin catalysts based on either nickel or aluminum.



G. BAZAN/UNIV. OF ROCHESTER

Short and sweet. With the help of boron and zirconium atoms, a new catalyst creates ultrashort polymers known as α-olefins under industrially friendly conditions.

"It's some very nice work," says Richard Kemp, a chemist at Union Carbide in Houston. "Nobody has come close to creating as pure a material as [the Rochester group]." Kemp notes that besides producing α-olefins more efficiently, the new metallocene works at ambient pressure, whereas current catalysts require high pressures. "That's a winner," says Kemp. "Anything you can do at atmospheric pressure is phenomenal," because it obviates the need for plants to install expensive high-strength reactors. Kemp and Guillermo Bazan—who led the Rochester team—are quick to point out, however, that the new catalysts are not ready for the factory floor just yet. Unlike the current variety, the new catalysts are difficult and expensive to produce, at least for now.

Metallocenes owe their finesse to their unique structure, in which a central metal atom is surrounded by a pair of five-membered carbon rings that can themselves be linked to other groups. The central metal atom is electron-hungry, which leads it to pull on the electron-rich parts of the olefin building blocks—simple hydrocarbons known as ethylenes—and draw them into the catalyst. Together, the rings and dangling groups force each ethylene to bind to the metal in a particular orientation. But the bond between the metal and the first carbon on the ethylene is highly reactive. This allows the next ethylene that is drawn in to insert itself between the first ethylene and the metal, forming the first link in the polymer chain.

In most metallocene catalysts, this chain growth continues on and on until the metal atom manages to yank an atom, usually a hydrogen, completely off the polymer, allowing the polymer to break free of the metal and stopping its growth. However, the chain is normally snipped only after the polymer has grown to great length. So Bazan and his Rochester colleagues Jonathan Rogers and Caroline Sperry looked for a way to speed up the process, so that chain growth would stop after two to 15 ethylenes—the length of an α-olefin.

That meant boosting the central metal's hydrogen-swiping ability. To do so, Bazan and his colleagues inserted a boron atom