Chemistry

A positive step for silicon chemistry

Scientists have made a novel form of silicon with potentially new properties to tap. A team of chemists at Northwestern University in Evanston, Ill., and Indiana University in Bloomington has created and identified the first stable silicon cation, a positively charged ion that has three bonds. Silicon naturally forms two, four, or five bonds.

The new silicon cation may lead to better strategies for synthesizing silicon-based materials, researchers believe.

For the past 50 years, chemists have aspired to make a form of silicon with three bonds. They believed this was possible because carbon, a close relative on the periodic table, can form a "carbocation," which also has three bonds and a positive charge. The highly reactive carbocation — an intermediate in many organic and biological processes — has helped researchers probe the mechanisms behind chemical reactions. Carbocations also serve as industrial catalysts.

But the silicon cation proved more difficult to make than the carbocation. It is more reactive and thus more fleeting. In the June 25 SCIENCE, the researchers describe how they trapped this elusive chemical species.

Led by Joseph B. Lambert of Northwestern University, the group made two key breakthroughs this past year. First, they discovered a good solvent that stabilized the cation. Toluene did the trick, although the researchers were surprised that a hydrocarbon solvent readily dissolved this charged molecule.

Second, they identified a negatively charged ion, called an anion, to pair with the cation. This anion doesn't react with the silicon cation, but prevents it from reacting with other chemicals. It plays a protective role because its negative charge is diffuse, spreading widely over its large molecular structure, which contains 20 fluorine atoms, Lambert notes.

Using X-ray crystallography, the researchers obtained an atomic-level picture of their quarry. They determined that it indeed holds the positive charge and is too far removed from the anion, at 4 angstroms, to be considered bonded.

Philip R. Boudjouk, a silicon chemist at North Dakota State University in Fargo, calls the work a "very important development in organometallic chemistry." He adds, "The silicon cation is quite a reactive species, so we should be able to do things with it that you normally can't do."

Boudjouk speculates that it may prove useful for catalyzing the formation of polymers. Already, the silicon cation appears to speed the process for making materials used in silicone products, such as lubricants and adhesives, Lambert reports.

CFC alternative: Recycled refrigerants

More than half the world's nations, including the United States, have agreed to halt their production of ozone-depleting chlorofluorocarbons, or CFCs, beginning in 1996 (SN: 12/12/92, p.415). Unfortunately, researchers have developed few environmentally friendly replacements for these refrigerants. However, CFCs might serve another 20 years if cleaned up and recycled, says Robert E. Kauffman, a chemist at the University of Dayton (Ohio) Research Institute.

Researchers assumed that recycled refrigerants wouldn't be up to par, but Kauffman's findings suggest otherwise. He studied refrigerants that spent years coursing through air-conditioning systems, picking up oils and acids along the way. He removed the oils and passed the remaining liquid through a filter containing beads of aluminum silicate zeolite crystals, which act as molecular sieves. The recycled refrigerants performed as well as new, he reported June 29 at a meeting of the American Society of Heating, Refrigerating, and Air-Conditioning Engineers. Moreover, the cleaning reduced their corrosiveness and thus their chance of causing leaks into the atmosphere, he says.

Earth Science

Devilish ice-age record

With a name like Devils Hole, it's no wonder this flooded fissure in Nevada keeps stoking the flames of discord. Some five years ago, researchers used the climate clues locked within Devils Hole to launch a debate over the cause of the ice ages. Now, the same evidence has come back to haunt them.

Over the millennia, the walls of Devils Hole have become plastered by layer upon layer of calcite, which contains information about rainfall changes in the area. This record first attracted attention in 1988, when scientists studying the calcite reported that the Devils Hole evidence refutes the Milankovitch theory, the standard explanation for the ice ages (SN: 12/3/88, p.356; 10/10/92, p.228).

Named after Yugoslavian mathematician Milutin Milankovitch, the theory holds that wobbles in Earth's orbit set the pace for the growth and disappearance of the great glacial sheets that have spread over parts of North America, Asia, and Europe every hundred thousand years or so. In the 1970s, research on oxygen isotopes in seafloor sediments provided strong support for the Milankovitch theory. But scientists who studied Devils Hole suggested that the timing of climate fluctuations recorded in Nevada did not correspond with orbital changes, indicating that some other factor must provide the pacemaker for the ice-age cycle.

Supporters of the Milankovitch theory are now using the Devils Hole record to support the orbital idea. In the June 10 NATURE, John Imbrie of Brown University in Providence, R.I., and his colleagues report that the changes recorded at Devils Hole contain hints of cycles lasting 100,000, 40,000, and 23,000 years. These periods match those of the orbital cycles, suggesting that such variations controlled the timing of climate changes at Devils Hole. Imbrie and his co-workers also show that the Devils Hole calcite and the seafloor sediments record inherently different aspects of the climate, which do not change in sync with each other. For that reason, the timing discrepancies between Devils Hole and the orbital shifts need not contradict the Milankovitch theory, they say.

A sound way to sense the sky

With massive loudspeakers aimed skyward, engineers are testing a new technique for taking the atmosphere's temperature — an approach that could eventually help meteorologists improve weather forecasts. The sound-based system provides temperature readings every six minutes and can fill gaps between the twice-daily measurements made by weather balloons, according to the National Oceanic and Atmospheric Administration (NOAA), which is developing the system.

The technique relies on a combination of loudspeakers and special Doppler radars that gauge the speed of winds in the atmosphere. By bouncing the radar off ascending acoustic waves, the system can judge the speed of the rising sound up to 1.5 miles in altitude. Because sound waves move faster through warmer air, the sound's speed provides a measure of atmospheric temperature.

The system does have some drawbacks. To get the most radar reflection possible, the speakers must emit a frequency that falls in the middle of the range of human hearing. This siren-like sound can be heard for several miles — a factor that precludes the use of this technique in populated areas, says Daniel Law, a NOAA engineer in Boulder, Colo.

NOAA engineers have installed the acoustic system at five of the 31 sites that house wind-profiler radars. Currently, they are running only two of the sound thermometers full-time; the others sit too close to farms to permit nighttime use. The team is evaluating the temperature data collected by the acoustic systems, but meteorologists have not yet had a chance to incorporate the information into their forecasts.