

Separating Isotopes by Switching Electrons

In general, there is little to distinguish two isotopes of a given element. One is slightly heavier than the other, but their chemical properties are almost identical. Consequently, methods for enriching uranium and separating isotopes have usually relied on differences in mass to achieve a separation. Now a group of researchers has discovered a significant chemical difference that could lead to efficient isotope enrichment.

The technique, developed by Gerald R. Stevenson and his colleagues at Illinois State University in Normal, depends on the observation that certain organic compounds bearing different isotopes vary in their ability to attract electrons in solution. This difference in electron affinity, as the property is called, makes it possible to separate molecules carrying one isotope from those carrying the other.

"Such processes, having unprecedented separation factors coupled with the advantages of working in solution, could make enrichment of a large variety of isotopic species much more practical than is the case today," Stevenson and his group report in the Oct. 9 NATURE. Related papers have appeared in recent issues of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

The researchers start with the com-

pound nitrobenzene dissolved in liquid ammonia. The nitrogen atom (N-14 or N-15) in each molecule may contain either 14 or 15 protons and neutrons. The addition of potassium to the solution provides a source of electrons. Some nitrobenzene molecules then pick up electrons to become singly charged negative ions, also known as radical anions. Surprisingly, molecules bearing N-15 are much more likely to attract electrons and become anions than those with N-14.

Evaporation of ammonia from the solution leaves behind a mixture of the neutral nitrobenzene and the potassium-anion salts. The nitrobenzene residue can then be distilled away, and the remaining salt chemically treated to turn it back into neutral nitrobenzene. This final product now contains a higher proportion of molecules with N-15 than it had before.

"The enriched mixture can be further enriched in N-15 simply by subjecting this new mixture repeatedly to the same process," the chemists say. "Starting from ordinary nitrobenzene containing 0.37 percent N-15 (natural abundance), it would take 16 passes through this procedure to produce a sample of 99 percent pure [N-15] nitrobenzene."

Stevenson has found similar effects for compounds in which deuterium replace

hydrogen and in which carbon-13 or radioactive carbon-14 replaces carbon-12. "We can take material that's not very radioactive and run it through a few cycles," says Stevenson, "and then we've got highly radioactive material."

Stevenson is interested in extending his method to other isotopes, including uranium-235 and uranium-238. "The first thing we have to do is to get the element that we're interested in into an organic molecule that will accept an electron," says Stevenson. Once a suitable "vehicle" is found, the rest of the procedure is relatively straightforward.

Other researchers are now looking into whether the effect also occurs when the molecules are in an electrochemical cell where they can pick up electrons directly. Using electrochemical techniques, chemist Angel Kaifer of the University of Miami in Coral Gables, Fla., has confirmed Stevenson's work on deuterium and hydrogen in anthracene molecules and is now trying to check the nitrobenzene results.

"Never in my life have I seen something like this," says Kaifer. "From an electrochemical point of view, as far as I know, this is the first observation of this effect."

John Bartmess of the University of Tennessee at Knoxville has looked at the same process in the gas phase, where neither solvent nor positive ions are present to interfere with the effect. "We are, in general, seeing the same sort of pattern," says Bartmess. "Most of the isotope effect that is observed is inherent to the structure of the radical anion."

Theoretical calculations also confirm that strategically located isotopes should have an effect on electron affinities. "There were certain earlier indications that ions, both positive and negative, have equilibrium effects," says Bartmess. "People had seen this before with other things." However, many assumed that solvent and positive-ion influences would swamp any isotope effects in solution.

Stevenson, says Bartmess, was the first to identify a chemical system that has potential practical value. "The nice thing about radical anions," he says, "is they're easy to make and easy to get rid of." That makes it simple to do a separation and end up with an isotopically enriched sample of the starting material.

"We're putting an emphasis on getting a good theoretical understanding of this effect," says Stevenson. "Experimentally, we want to work our way into metals." Meanwhile, the university has applied for a patent on Stevenson's technique. Several chemical companies that manufacture medical products have already shown an interest in the process.

—J. Peterson

