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Shaken, Not Stirred

Creating organic compounds without solvents

As often happens in science, a group of Ames Laboratory researchers didn't set out to discover a revolutionary process to create organic compounds. Study in another area prompted a question and a "let's-give-it-a-try" response.

As a result, their findings that organic compounds can be formed in solid state marks a major advance in both materials science and chemistry where the two fields overlap. The discovery means that environmentally harmful solvents, such as benzene, dichloromethane and others, could be removed from many of the chemical processes used to produce thousands of consumer and industrial products. The initial cost-savings for the solvents alone would be substantial, but when combined with the reduction or elimination of disposal costs for the spent solvents and minimization of chemical waste streams, the overall benefits could be enormous.

Balls replace solvents

The discovery centers on ballmilling, a process routinely used to alloy various metals. Simply stated, the component metals to be alloyed are placed inside a hardened steel vial along with balls of varying sizes. The sealed vial is then shaken vigorously for extended periods of time. Mechanical energy going into the system is transferred to the materials, eventually combining them at the molecular level to form the new alloy.

Organic materials have very different crystal structures, so they don't readily combine in solid state when mixed together; typically they must be dissolved to break down their crystallinity. Once the materials are in solution, they can be combined and the chemical reaction takes place. The resulting product is then separated out.

Given their expertise in alloying various materials, Pecharsky and a fellow researcher, Ames Lab associate scientist Viktor Balema, decided to *continued on page 2*

A close-up shows a hardened steel vial and the balls used to process the materials. The vial fits in the cage of the mill, which operates similar to a paint shaker at a paint store.

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explore if ballmilling could take the place of solvents in carrying out organic chemical reactions in solid state. Shaking up the materials was easy. The problem was how to tell whether the reaction had indeed taken place during mechanical processing of the solids.

One major tool typically used to study a material's crystal structure is diffraction analysis. X-rays — short wavelength electromagnetic radiation — shone through a material will form a specific diffraction pattern dependent on the crystal structure of the material. This usually allows researchers to identify the solid material based on the spectrum displayed.

"But since our experimental approach is mechanochemical, it reduces the particles to very small size and induces plenty of strain and stress," Pecharsky says. "Essentially, what we end up with is either poorly crystalline materials or materials that aren't crystalline at all, and diffraction techniques are nearly useless."

NMR tracks reactions

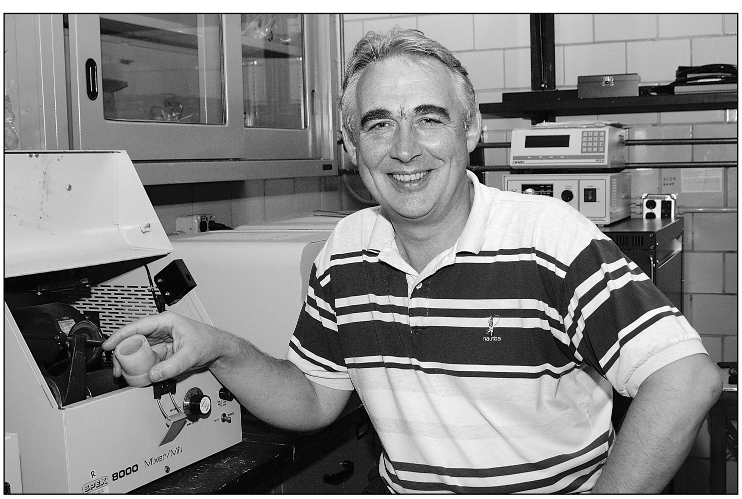
For answers, Pecharsky and Balema turned to Ames Lab colleagues, physicist Marek Pruski and chemist Jerzy Wiench, leading experts in solid state nuclear magnetic resonance spectroscopy, known as NMR. In NMR, a strong magnetic field is used to split the energy levels of the atomic nuclei in the material being studied.

"The transition frequency that corresponds to the splitting identifies the nucleus and the local environment in which the given nucleus finds itself," Pruski says. "In other words, by monitoring the transition frequency, we can fingerprint the specific material."

NMR proved to be perfect for verifying the experimental results. Using materials that produce well-known and well-documented reactions when carried out in solution, Balema and Pecharsky combined these prototype materials in the ball mill and took the resulting products to Pruski and Wiench. With a limited number of possible end products, they were able to quickly match the NMR of the experimental products with commercially prepared samples.

"The spectra that we collected indicates that the processes do occur in solid state," Wiench says, "ruling out the possibility that heat generated during processing melts the materials, permitting the reaction to take place in a liquid state." Another advantage is that NMR testing is non-destructive and doesn't require any prior or further processing of the material. According to Wiench, this helps eliminate any chance that other factors might influence the reaction.

Viktor Balema loads material into a ball-mill vial in a glove box to prevent possible contamination of the sample prior to processing.



Vitalij Pecharsky holds a ball-milling vial used to process materials. The mill vigorously shakes materials for extended periods of time.

High yields, one pot

Not everything the team ran through the ball mill was a success, but nearly all of the discovered transformations previously performed exclusively in solution were found to be exceptionally efficient and selective in the solid state. "I would never have believed that solvents could be excluded from all these reactions if I hadn't done it myself," says Balema, adding that milling times varied from one hour to 25 hours, depending upon the reaction being examined.

Another valuable discovery is that the reactions can be carried out consecutively, or as "one-pot" processes, when components required for performing a reaction in stages are ball-milled together in the same vial. "Remarkably, a 'one-pot,' Wittig-type reaction between phosphines, organic halogenides, aldehydes or ketones, and a base is impossible in a solution, but it has been successfully carried out in a mill without a solvent," Pecharsky says.

To date, the group has operated on a shoestring budget, borrowing research time to carry out the testing. Materials costs have been minimal, according to Pecharsky, and the testing has used existing equipment.

"If we were to go into some more adventuresome experiments," Pruski says, "we would need to invest more time and money in special accessories. We've been able to work around those problems up to now."

Though they only published their findings in the June issue of the *Journal of the American Chemical Society*, Pecharsky indicates that their work has already been cited by another group looking into mechanochemistry.

"It's different work and a different reaction," he says, "but it's all mechanochemistry." They were also successful in carrying out organic reactions in solid state with quite high yields. "Now that we've shown that it can be done without solution, maybe mainstream organic chemists will try it — and most likely succeed, too, which is good. That's how science is done these days. You can't do it alone," says Pecharsky.

Echoing that sentiment, Pruski says the Ames Laboratory effort is truly a multidisciplinary collaboration. "Even though we're in different programs, it's been a good symbiotic collaboration on science at a very basic level," he says. "It's the way a national lab ought to function." ■

~ Kerry Gibson