X-ray method solves mystery of metallic ammonia

Researchers study how solvated electrons behave inside the classic reagent used in Birch reductions

by Mark Peplow, special to C&EN

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When alkali metals like sodium dissolve in liquid ammonia, they produce a colorful spectacle that has puzzled and delighted chemists for centuries. The metals release electrons that give the solution a deep blue hue—first seen by Humphry Davy in 1808—which eventually transforms into a lustrous bronze as more metal dissolves.

The blue solution's solvated electrons act as a powerful reducing agent, used in reactions such as the Birch reduction to convert arenes into cyclohexadienes. But the molecular details behind the transition from blue to bronze, which is accompanied by a dramatic increase in the solution's electrical conductivity, have remained a mystery.

Now chemists have directly observed how the behavior of solvated electrons changes during this transition, and used computational modeling to flesh out the story (Science 2020, DOI: 10.1126/science.aaz7607).

The team studied the solvated electrons with a technique called X-ray photoelectron spectroscopy. It uses X-rays to bump electrons out of a sample, and then measures the kinetic energies of the ejected electrons to reveal their initial energetic states. The method requires an ultra-high vacuum, because any stray gas molecules might deflect the fleeing electrons away from the detector. So the researchers cunningly delivered their volatile metal-ammonia solutions in microjets roughly 100 µm wide, to avoid forming too much disruptive ammonia vapor. The solutions contained lithium, sodium, or potassium, at varying concentrations.

At low concentrations of dissolved metal, each solvated electron is contained in a loose shell of 10-12 ammonia molecules, and occupies a region that is roughly 8 Å wide. "The solution has a very distinct blue color because these electrons strongly absorb in the red part of the spectrum," says Pavel Jungwirth at the Czech Academy of Sciences, who was part of the research team.

Adding more metal increases the density of solvated electrons, prompting the electrons to form pairs within each ammonia cavity. At still higher concentrations, their energy levels gradually blur together to form a conduction band seen in metals. Ripples in this sea of electrons, known as plasmons, are ultimately responsible for the solution's bronze color.

Even before the solution visibly turns bronze, there are characteristic peaks in the photoelectron spectrum indicating that a conduction band and plasmons have formed.

“It’s an unequivocal signature of a metal, because you cannot see it if you have chemically-isolated electrons,” Jungwirth says.

“The fact that they saw these metallic signals in the spectrum before the color change happened was really fascinating,” says Christine M. Isborn, a theoretical chemist at the University of California Merced, who was not involved in the research. “It’s metallic, even though our eyes don’t see it as metallic yet.”

For an encore, Jungwirth says that his team has already turned its X-rays onto a much stranger target: metallic water.

Water is known to host solvated electrons, although the solution is less stable than a metal-ammonia mixture. In principle, using an alkali metal to increase the density of solvated electrons in water should also generate a metallic state, just as it does in ammonia. But alkali metals react with water, often violently, which poses a major experimental challenge.

Nevertheless, Jungwirth says his team has managed to combine a droplet of sodium-potassium alloy, which is a liquid at room temperature, with water vapor. This forms a thin skin of solvated electrons around the metal droplet that persists for a few seconds — long enough for the team to confirm the solution’s metallic status by optical and photoelectron spectroscopy.

These results are not yet published, and Jungwirth is unsure whether metallic water will have any practical uses. “But it’s amazing that you can convert water into a metal, and you can actually do it very simply,” he say. “The perfect use, for me, is that if I show this to high school students, there’s a good chance some of them will study chemistry.”

Scientists finally solve the mystery behind a 100-year-old chemistry experiment

By Stephanie Pappas, published July 01, 2020

Scientists may finally understand the mysterious transition behind a century-old chemistry experiment. The details of this transformation, in which adding electrons to a bright blue ammonia solution morphs it into a lustrous, metallic bronze, have long eluded scientists.

The new study reveals the subtle details of this change, and shows that this transformation is gradual, rather than sudden. "What we've done successfully is that we've pretty much understood how these solutions behave at a wide range of concentrations using a microjet technique," said study co-author Ryan McMullen, a doctoral student in chemistry at the University of Southern California. This technique, which involves shooting hair-thin streams of the solution through a vacuum, has not been used on the lustrous liquid before.

And the discovery could open up new types of reactions in organic chemistry in the future, McMullen told Live Science.

What is a metal?

Metals are a diverse group. Some, like lithium, are light enough to float, while others, like lead or osmium are extremely dense. Some require incredibly high temperatures to melt, while others melt easily (Mercury, for example, melts at minus 38.3 degrees Celsius, or minus 37.9 degrees Fahrenheit). Ultimately, what metals have in common is their ability to conduct electricity at absolute zero, the point at which molecular movement from heat essentially halts. But how do some nonmetals transform into metals? In a new study, researchers answered that question by adding metals to liquid ammonia.

First, the researchers condensed ammonia, which is a gas at room temperature, into a liquid by cooling it to negative 27.4 F (minus 33 C). They then added either sodium, lithium or potassium, which are all alkali metals. (Rather famously, these metals react explosively when submerged in water.) The experiments were done in collaboration with scientists from the Czech Academy of Sciences and the Fritz-Haber Institute of the Max Planck Society in Berlin, as well as researchers in Japan and France.

The result was an expected reaction: The liquid ammonia pulled electrons from the metal. Those electrons then became trapped between the ammonia molecules, creating the so-called solvated electrons the researchers hoped to study. At low concentrations, the result was a blue, non-metallic liquid. As the solvated, or trapped, electrons piled up, though, the solution transitioned to shiny bronze.

The next challenge was to investigate how the solvated electrons behaved at different concentrations. This involved shooting a microjet of the solution — about the width of a human hair — through a beam of synchrotron X-rays, which are high-energy X-ray beams. The X-rays excited the solvated electrons, causing them to hop out of their liquid cage of ammonia molecules. The researchers could then measure how much energy it took to release the solvated electrons.

The researchers found that the greater the concentration of solvated electrons, the more the pattern of energy release matched what is seen in a metal. Here's what that means: If you graph the amount of energy required to free electrons from their liquid ammonia cage, metals typically have what's called a "Fermi edge," a very abrupt transition, McMullen said. At lower concentrations of solvated electrons, this energy-release graph looks more like a rounded hill. Only at higher electron concentrations did this Fermi edge emerge. The edge reflects how much energy electrons have at a given temperature, McMullen added.

"When you increase the concentration to the metallic range then you see, this wonderful pattern emerges that is very, very characteristic of a metal," McMullen said.

The results were interesting because they showed that the metal-like liquid created by combining alkali metals and ammonia actually is a metal on a fundamental physical level, he said.

"It is a genuine metal, it's not something that just looks like one," McMullen said.

Lower-concentration solvated electrons are used in a type of reaction called a Birch reaction, which adds electrons to molecular structures called aromatic rings. This kind of reaction was used in the manufacture of the first oral contraceptive pills in the 1950s, McMullen said. By understanding how solvated electrons work at high concentrations, researchers can potentially find new kinds of chemical reactions, he said. For example, they might excite the solvated electrons with beams of light to get them to behave in new ways.

"If you tickle the electrons a bit so that they're more energetically excited, you can start looking at some crazy reactions that would never otherwise happen," McMullen said.

The researchers reported their findings June 5 in the journal Science.