

## CHAIN, CHAIN, CHAIN

### WITH EXPERIMENTS BACKED UP BY COMPUTATION, SCIENTISTS FOR THE FIRST TIME OBSERVE THE MOLECULE-BY-MOLECULE TRANSFORMATIONS OF A MOLECULAR CHAIN-REACTION



**Free radicals can cause explosions.** This is not only a socio-political statement (and theme of a Dostoevsky novel), but also a chemical phenomenon. "Flames and explosions that occur, usually in the gas phase, involve what are known as 'free radical chain reactions,'" explains John Yates, now a chemistry professor at the University of Virginia, "a class of reactions that's been known for maybe 90 years."

While scientists have known of these molecular chain reactions, they had never observed the atom-by-atom details of how the molecules break into "free radicals" — molecules with an unpaired electron, which makes them highly reactive — and form new bonds. Recent work by Yates and colleagues, reported in *Science* (December 2008), has rendered the unseeable seen. In a fruitful collaboration between laboratory experiment and supercomputing, Yates — formerly at the University of Pittsburgh, founding director of its Surface Science Center (SSC), and graduate student Peter Maksymovych (now a Wigner fellow at Oak Ridge National Laboratory) teamed with University of Pittsburgh theoretical chemist Ken Jordan and Dan Sorescu of the Department of Energy's National Energy Technology Laboratory.

Yates and Maksymovych used the SSC's ultra-high vacuum scanning tunneling microscope (STM) to induce a reaction in a chain of dimethyldisulfide ( $\text{CH}_3\text{SSCH}_3$ ) molecules self-assembled on a surface of gold. The sulfur-sulfur bonds broke and reformed into new DMDS molecules via a propagating chain reaction. To follow-up on these intriguing results, Jordan and Sorescu did theory-based computations on PSC's

BigBen. The computations provided new insight and support the conclusion of a free-radical chain reaction, the first time that such a reaction has been produced with molecules on a surface.

"This is the first time anyone has ever seen a chain reaction molecule-by-molecule," says Yates. "From a historical point of view, this well established type of chemical reaction, previously known only from indirect measurements in the gas phase, has now finally been seen when you pin the molecules to a surface."

Jordan concurs. "What's new is showing that you can get a chain reaction on a surface." He credits the collaboration between experiment and computation. "In many grand challenge problems — and I think this is true of a lot of the work done at PSC — significant progress occurs because computational and experimental researchers have teamed up."

"This was a great example of a collaboration involving the resources of two major centers — the University of Pittsburgh Surface Science Center and the Pittsburgh Supercomputing Center," says Yates. "It was a vibrant collaboration between theorists and experimentalists."

The new findings suggest practical applications related to nanolithography, a light-induced process by which thin, electron-conducting pathways are laid down on semiconductor surfaces in the manufacture of microchips. "The broad field of photochemistry on surfaces," the researchers conclude in *Science*, "will now have to account for chain processes in surface reaction mechanisms."



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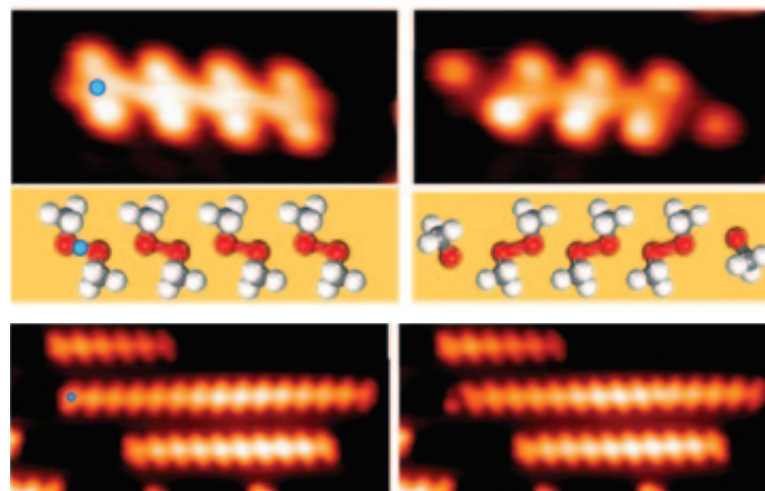
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## CHAIN REACTION ON A SURFACE

These STM images show the before and after (reacted and unreacted) results of electron-induced dissociation of a single  $\text{CH}_3\text{SSCH}_3$  molecule and the self-assembled chains on a gold surface. The schematic ball and stick models are shown beside their related STM images. An introduced electron (blue dot) initiates the reaction.



Maksymovych and Yates first performed the STM experiment on a single DMDS molecule, then two molecules, then four (upper right), then a 15-unit chain. This last experiment (lower right) initiated a chain reaction involving 10 of the 15 DMDS molecules in a row, and produced nine new molecules before the gold surface quenched the reaction. "The self-assembled molecular structure," wrote the researchers in *Science*, "thus redirects the energy flow toward a chemical chain reaction involving multiple steps, rather than rapid dissipation into the metal bulk."

## SOLID GOLD CHEMISTRY

The secret of this step forward in the chemistry of chain reactions was to confine the reaction to a surface — in this case a surface of solid gold. Actually a little ball of gold presenting single crystal facets on the end of a gold wire, explains Yates. As the part of a solid exposed to the world, a surface is a dynamic place for interactions — such as oxidation, corrosion and catalytic reactions, among others — and a discipline known as "surface science" has grown up around studies of such phenomena.

Before the DMDS results, scientists doubted that a propagating chain reaction could be sustained on a surface. "The traditional view," says Jordan, "is that the excess energy is going to dissipate too rapidly into the atoms in the surface and that this would kill the reaction."

Maksymovych used the SSC's state-of-the-art STM to introduce DMDS molecules onto the gold surface. Yates and Maksymovych chose to work with DMDS because similar molecules were known to self-assemble into chains under the right conditions.

You can think of a DMDS molecule as dumbbell-shaped, with methyl groups ( $\text{CH}_3$ ) as the heavy ends joined by the S-S bond. Through the self-assembly that occurred as the DMDS molecules were deposited, the dumbbells line up side-by-side on the gold surface, leaning to the left. Maksymovych then used the tip of the STM probe to inject electrons into the first DMDS molecule. A short time later, the DMDS molecules were reformed, still in a chain but now leaning to the right, opposite of their starting orientations.

To a non-scientist it may have looked like the molecules did a group shift, left to right, but Yates and Maksymovych saw something else. Their analysis of the STM images revealed that the reformed DMDS

molecules were not only tilted but also offset to the right, strong evidence that chemical bonds were broken in the process. From this and other evidence, the scientists deduced this scenario: an electron splits the first S-S bond, creating two  $\text{CH}_3\text{S}$  radicals. One bonds to the gold surface while the other attacks and splits the DMDS molecule next to it in the chain, forming two more radicals. Two of the three then bond to form a new DMDS, while the third radical repeats this step on the next DMDS down the line.

Like a patterned dance figure in two lines of dancers, the molecules broke apart and reformed with different partners down the chain. "It's like unzipping a zipper," says Yates, "a repetitive process down the chain. It's really beautiful — never been seen before, that's for sure."

## THE CLINCHER: LOWER ENERGY BARRIERS

Why does this chain reaction happen when no one thought it would, and how can the experimentalists know for sure that it happened as they believe it did? To look more deeply, Jordan and Sorescu went to work to compute the energy changes during the course of the reaction. When graphed, the energy trajectory of a reaction can look like a roller coaster, with peaks representing energy barriers — in this case, the energy needed to break the bond between the two sulfur atoms of DMDS. "The experimental work does not give you the energy barriers directly," says Jordan, "and this is one of the ways that theory — computational work — is very useful."

Their computations relied on density-functional theory (DFT), for which Walter Kohn shared the 1998 Nobel Prize in chemistry (with Carnegie Mellon's John Pople). One of the most used methods in

quantum chemistry, DFT makes it possible to calculate energy barriers and other electronic properties for reactions such as this one, though the computational demands are daunting. "Doing the density functional calculations," says Jordan "is not something you run on your notebook computer. You need a powerful supercomputer."

Using software called VASP (Vienna Ab-initio Simulation Program) and 64 processors of PSC's BigBen system, Jordan and Sorescu calculated the electron density and energy of the DMDS molecules on the gold surface. Their simulation started with a 188 atoms representing the gold surface, together with a chain of self-assembled DMDS molecules to replicate the conditions of the experiment.

The computations showed that the energy required to break the S-S bond in a DMDS chain on a gold surface is much lower than that required to break the S-S bond of an isolated DMDS molecule. In the chain, the S-S bonds of the neighboring DMDS molecule allowed the reaction to proceed with an energy barrier five times lower than that for an isolated molecule. "A change of five in a barrier," says Jordan, "is a big effect."

The low energy barriers validate the conclusion that the reaction moved down the chain's length rather than reacting with the gold surface — and confirm Yates's zipper analogy. "Here we have this self-assembled structure and the bodies are all nestled close together in a certain configuration," he explains, "and now the chain reaction is encouraged by the fact that everything is in the right place to make it unzip."

As the scientists observe in their paper, this first convincing evidence of propagating surface chain reactions could affect microchip manufacturing.

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"It could very well be," says Yates, "that when you get down to very thin photoresists, no thicker than a single layer, then suddenly these organized reactions that you hadn't expected will take place."

There's much yet to be learned about such reactions, says Maksymovych. "After all," he observes, "biological life is the ultimate example of functionality that arises out of self-assembled molecules. This reaction is also a seminal example of how simple self-organization can give rise to non-trivial, chemical functionality that doesn't exist in the individual building blocks." (TP)

## MORE INFORMATION

[www.psc.edu/science/2009/nanoassembly/](http://www.psc.edu/science/2009/nanoassembly/)

## SHIFT TO THE RIGHT

This surface lattice of the  $\text{CH}_3\text{SSCH}_3$  tetramer (four molecules) before and after the reaction shows that the product molecules (right) have shifted .25 nm (nanometre) toward the right.

