Researchers control chemical reactions one molecule at a time

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Scientists at the University of California, Riverside showed that L. P. Hammett's 1937 prediction of the strength of different acids is directly transferable to the activation of individual molecules on metal surfaces using the tip of a scanning tunneling microscope (STM) as a nanoscale actuator.

Hammett's original prediction is a cornerstone of physical organic chemistry, which laid the foundation for many quantitative structure activity relationships that are now widely used in fields such as drug design and environmental toxicology.

Ludwig Bartels, an assistant professor of chemistry at UCR, used an STM to demonstrate that Hammett's concepts still hold true at a scale where molecules are individually guided one at a time and step-by-step through a chemical reaction.

An STM acquires the height profile of a surface at the atomic scale by guiding a needle across the surface in a process similar to how a blind person reads Braille. The dots it can resolve are no larger than individual atoms or molecules. Thus, it enables scientists to see images of individual atoms and molecules on metal and semiconductor surfaces. The same needle tip used for scanning can inject tailored electrical pulses into molecules that render portions of them reactive by modifying their chemical make up.

Bartels led a team of researchers whose findings are published in this

week's issue of the Proceedings of the National Academies of Science in a paper titled Measurement of a Linear Free Energy Relationship One Molecule at a Time. Co-authors with Bartels are UCR graduate student Ki-Young Kwon, who performed the data analysis and interpretation, as well as UCR postdoctoral researchers Bommisetty Rao, who performed the bulk of the experiments, and Anwei Liu, who developed the Scanning Tunneling Microscope used for the experiments.

In detail, Bartels and his team found that identical electrical pulses activate the thiol group of benzenethiol molecules more or less readily depending on the nature and the position of substituents (such as bromine atoms or methyl moieties) on their benzene ring.

The activity of thiol groups is used to anchor molecules to metal electrodes in virtually all molecular electronics schemes proposed so far. The benzenethiols used in Bartels' study comprise a good model system for molecules used in molecular electronics and these findings may support future nanoscale assembly of "molectronic" devices - using molecular systems in electronics instead of silicon.

In 2000, researchers - including UCR's Bartels - found that the STM can assemble individual biphenyl molecules from elementary building blocks (iodobenzene) by a sequence of activation of the building blocks and transfer of the activated blocks to close proximity so that they can bind to one another chemically. But because scientists lacked control of the activation of potential building blocks, little progress has been made toward the assembly of larger and more useful molecules.

The new technique now shows how scientists can fine-tune the reactivity of groups of molecules. "Ultimately, this may guide us how we can modify the linking groups in our starting molecules so that we can activate them separately, which will then allow us to activate one group, attach another molecule and, after that is accomplished, activate another

group, so that we can attach a third molecule, and so on...," Bartels said.

The new finding offers a route to the design of building blocks whose reactivity is tailored to optimize the atomic-scale construction of complex and functional molecules on surfaces.