Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

Atom by Atom, Bond by Bond, a Chemical Reaction Caught in the Act. Scientist capture first-ever high-resolution images of a molecule as it breaks and reforms chemical bonds. The achievement is published in Science.

Taking an image of an individual molecule while it undergoes a chemical reaction has been deemed one of the holy grails of chemistry. Scientists at the University of Berkeley and the University of the Basque Country (UPV-EHU) have managed, for the very first time, to take direct, single-bond-resolved images of individual molecules just before and immediately after a complex organic reaction.

The images of this outstanding research work enable appreciating individual carbon atoms and the bonds between them in a single molecule, as well as the processes of the rupture and creation of these bonds, as clearly as in a textbook diagram. The researchers report their results online in the May 30, 2013 edition of *Science Express* will be published in the next print issue of Science. The first author of this work is Dr. Dimas Garcia de Oteyza, who has just been reincorporated into the Material Physics Center, a joint CSIC-UPV/EHU center, after a postdoctoral term in Berkeley. Before Berkley, he was also postdoc at the Donostia International Physics Center (DIPC). This research is a collaboration between the groups of Felix Fischer (Department of Chemistry at Berkeley), Michael Crommie (Department of Physics at the same university) and Ángel Rubio (Professor at the UPV/EHU and researcher at the CSIC-UPV/EHU Material Physics Center and DIPC).

Organic chemical reactions are, in general, fundamental processes that underlie all biology, as well as highly important industrial processes, such as the production of liquid fuel. The structural models of molecules that we have traditionally relied on to understand these processes come from indirect measurements averaged over an enormous number of molecules (in the order of 1020) and from theoretical calculations. Nobody has ever before taken direct, single-bond-resolved images of individual molecules right before and immediately after a complex organic reaction.

“The importance of our discovery is that we were able to image the detailed microscopic structures that a molecule can transform into on a surface, thus allowing us to directly determine the microscopic atomic motions that underlie these chemical transformations”, explained Ángel Rubio. More specifically, researchers were able to record single-bond resolved images of an oligo-enediyne (a simple molecule composed of three benzene rings linked by carbon atoms) deposited on a flat silver surface. They used a technique called non-contact Atomic Force Microscopy (nc-AFM), based on an instrument with an extraordinarily sensitive tactile probe. This AFM uses a very fine needle that can sense even the smallest atomic-scale bumps on a surface in much the same way that you would use the tip of your fingers to read/feel a word written in Braille. Given that the oligo-enediyne molecules studied are so small (~10–9 m) the tip of the nc-AFM microscope was configured to end on a single oxygen atom. This oxygen arises from a single carbon monoxide (CO) molecule adsorbed onto the AFM microscope tip, which acts as an “atomic finger” in tactile reading.

By moving this “atomic finger” back and forth along the surface over the studied molecule they could detect not only the individual atoms and their precise positions within the studied molecule but also the chemical bonds between these atoms. Recent advances in this microscopy technique have made it so precise that we can even distinguish the bond order between carbon atoms (single or double or triple bonds). The resulting images bore a startling resemblance to the textbook diagrams used to teach chemistry, except here no imagination is required. Upon heating the underlying surface, a chemical reaction that is closely related to “cyclisations” is induced. Cyclisations, discovered by Berkeley Professor Bergman in the early 1970s, cause carbon atoms linked in chains to “fold up” into closed-ring formations (aromatic rings). “The images we recorded after the reaction clearly show how new chemical bonds are formed and how atoms within the molecule rearrange to form new structures”, explained Dimas Garcia de Oteyza. The results have been interpreted and analysed microscopically thanks to theoretical simulations carried out by Prof. Rubio’s group.

The nc-AFM microscopy provided striking visual confirmation of the mechanisms and the unexpected results reinforced the promise of this powerful new method for building advanced nanoscale electronic devices from the bottom up.

Apart from achieving striking visual confirmation of the microscopic mechanisms that underlie these synthetic organic chemical reactions, the unexpected results of the experiment reinforced the promise of this powerful new method for building advanced nanoscale electronic devices from the bottom up and manufacturing new, high-precision customised materials at a nanometric scale.

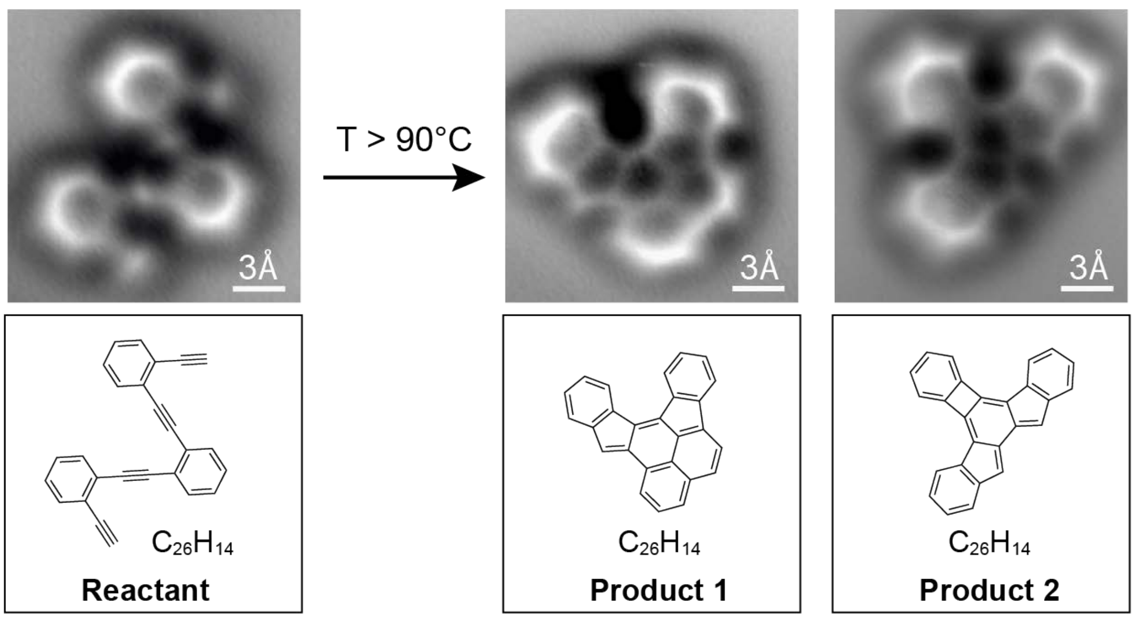

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Figure: The original reactant molecule resting on a flat silver surface, is imaged both before and after the reaction, which occurs when the temperature exceeds 90 degrees Celsius. The two most common final products of the reaction are shown. The images made by a noncontact atomic force microscope reveal the positions of individual atoms and bonds. The three-angstrom scale bars (an angstrom is a ten-billionth of a meter) indicate that both reactant and products are about a billionth of a meter across.

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