Probing hydrogen catalyst assembly

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Biochemical reactions sometimes have to handle dangerous things in a safe way. New work from researchers at UC Davis and Stanford University shows how cyanide and carbon monoxide are safely bound to an iron atom to construct an enzyme that can generate hydrogen gas. The work is published Jan. 24 in the journal *Science*.

Producing hydrogen with catalysts based on abundant metals, such as iron, is key to hopes of using hydrogen to replace carbon-based fuels. But before you can make hydrogen, you have to make the catalyst that enables the reaction –something bacteria have been able to do for millennia.

Jon Kuchenreuther, a postdoctoral researcher working with Professor Dave Britt, project scientist Simon George and colleagues at the UC Davis Department of Chemistry, with James Swartz and colleagues at Stanford, used a variety of analysis techniques to study the chain of chemical reactions that assembles these catalysts based on clusters of iron and sulfur atoms adorned with cyanide (CN) and carbon monoxide (CO) molecules.

"How does biology make these complicated active sites?" Britt said. "You can't release cyanide or carbon monoxide into the cell. It turns out that it's formed and kept on iron throughout."

In work published in *Science* last year, the researchers showed that the amino acid tyrosine first binds to the iron/sulfur cluster, and is then split by the enzyme HydG to create a radical. The new paper picks up the

story from there, showing that carbon monoxide and cyanide derived from the splitting of tyrosine, remain bound to the same iron atom as the tyrosine radical is removed. This iron/cyanide/carbon monoxide structure becomes part of the final cluster.

The team principally used a technique called Fourier Transform Infra Red spectroscopy to follow the process. FTIR measures vibrations in bond length, and both cyanide and carbon monoxide show strong signals with this method.

Metal atoms in biological molecules are usually bound to large structures, like amino acids or heme groups, Britt said. For metals to be bound to small molecules, like carbon monoxide and cyanide, is "some unusual chemistry by itself," he said.

More information: "The HydG Enzyme Generates an Fe(CO)2(CN) Synthon in Assembly of the FeFe Hydrogenase H-Cluster" *Science*, 2014.

Provided by UC Davis