Researchers confirm elusive structure of powerful oxidizing intermediate 'Q'

January 22 2015, by Erin Mchenry

University of Minnesota researchers have identified the structure of the key intermediate "Q" in the enzyme methane monooxygenase (MMO), which converts methane (natural gas) and oxygen into methanol and water.

John Lipscomb, Ph.D., professor in the Department of Biochemistry, Molecular Biology and Biophysics at the University of Minnesota partnered with a team of researchers at Michigan State University on the project. It was published this month in *Nature*.

The study confirms that Q, one of the most powerful oxidizing intermediates occurring in nature, has a diamond-shaped core consisting of two highly oxidized iron atoms connected by twin, single-oxygen atom bridges.

Lipscomb and other scientists had hypothesized this molecular makeup before, but this is the first scientific proof of the structure. Historically, observing the core has been difficult at best because Q's lifespan within MMO's catalyst cycle is just a few seconds. Methane is also one of the hardest bonds to break.

To determine the core, researchers used newly developed time-resolved resonance Raman vibrational spectroscopy to measure expansion and contraction motions within the diamond core. By making the measurements in a continuously flowing stream of MMO, the researchers could accumulate Q's weak visible spectrum for hours despite its short lifetime. The long continuous flow required 40 grams of the enzyme, which required almost one year to purify.

"Scientists have been studying Q for 20 years," said Lipscomb. "Now we know its molecular structure, and this will hopefully become a stepping stone for researching possible uses for methane in bioremediation, transportable biofuels, and chemical products."

This discovery also allowed researchers to identify the point in the MMO cycle where atmospheric O2 split into oxygen atoms, one of which is transferred into methane to make methanol.

A tremendous amount of energy is released when the methane bond is broken, making it an ideal fuel. However, it is difficult to transport, especially outside of the U.S. Converting methane to liquid methanol makes it easy to transport and a good alternative to petroleum for energy. Methanol is also often used in the development of many drugs, chemical processes, and synthetic products.

Other enzymes, including RNR (the enzyme that provides the building blocks of DNA), are likely to contain similar diamond core structures. Lipscomb hopes understanding one diamond core could provide the tools required for studying other similar structures.

The possible applications are countless, but only speculation right now. Lipscomb plans to continue studying Q and MMO, particularly the other intermediates in the reaction cycle. He hopes researchers and physicians will take the results and apply them to other projects studying enzymes, biofuels, drug discovery, and related sciences.

More information: "Structure of the key species in the enzymatic oxidation of methane to methanol" *Nature* (2015) DOI: 10.1038/nature14160

Provided by University of Minnesota