Watching particles' jekyll-to-hyde transformation

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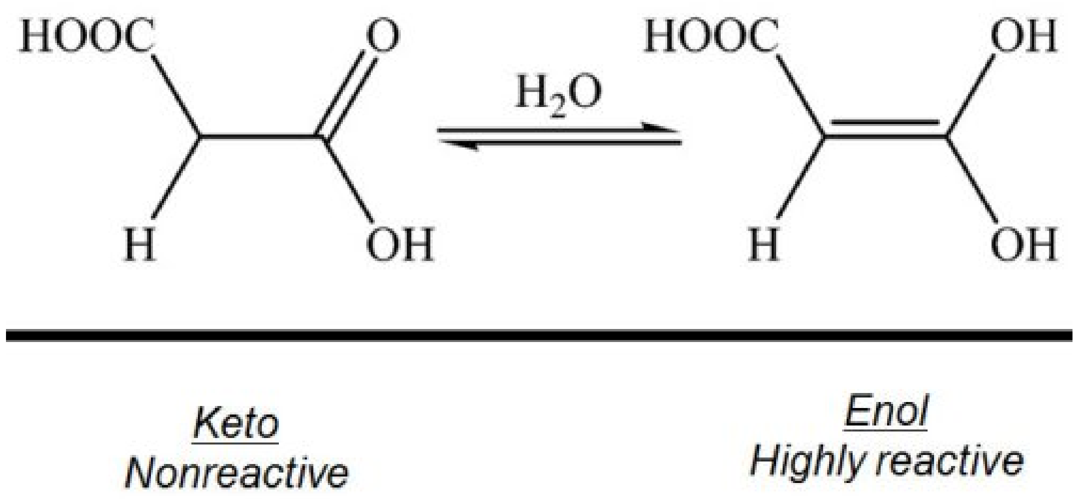
Whether the abundant atmospheric specie malonic acid stays in a stable keto form or twists into a highly active enol form depends on the amount of water it finds in the atmosphere, according to researchers at the University of Iowa and Pacific Northwest National Laboratory.

(PhysOrg.com) -- Whether a common atmospheric particle stays in a stable form or twists into something else depends on the amount of water it encounters in the atmosphere, according to scientists at the University of Iowa and Pacific Northwest National Laboratory. This result for malonic acid challenges conventional wisdom; the results are based on the complementary experiments conducted at two Department of Energy user facilities in a collaborative project facilitated through PNNL's Chemical Imaging Initiative.

Managing today's fossil-fuel-based energy infrastructure for both economic and environmental health requires controlling the fate and transport of ubiquitous particles produced by combustion engines and other sources. Traditional approaches, which assume that the particles behave the same way in the air as they do in bulk aqueous solution, have created some faulty assumptions. The chemical imaging technique and subsequent study correct several of those assumptions, allowing scientists to work with more accurate, direct observations of these troublesome particles. This information could not have been obtained with conservative approaches.

"There were no means to probe in situ chemistry of individual particles as they take up water in the atmosphere," said Dr. Alexander Laskin, a chemist within PNNL's Chemical Imaging Initiative. "The X-ray spectro-microscopy technique allowed us to watch as the particles changed between the nonreactive and highly reactive forms."

It begins with malonic acid, one of the most abundant carboxylic acids in the atmosphere. This molecule exists in two forms called keto and enol that differ only with respect to the position of one of the hydrogen atoms . The two forms co-exist in equilibrium, and there is no physical or chemical way to separate these two forms. With respect to their chemical reactivity, the keto form is stable and not very reactive, while the enol form is highly reactive. The common wisdom was that, in the atmosphere, the dominant form would be the keto form, the same as in aqueous solution. However, the team found that the aqueous chemistry results are not applicable in this case.



An abundant atmospheric species, malonic acid transforms from the stable, nonreactive keto form to the highly reactive enol form at elevated relative humidity. The reactive enol form is 4 to 5 orders of magnitude more abundant in the atmosphere than was expected from aqueous chemistry.

The team's approach began at EMSL, a DOE national scientific user facility at PNNL. Suman Ghorai and Prof. Alexei Tivanski of UI examined ensembles of malonic acid particles, characterizing hundreds of particles at a time using EMSL's optical microscopy and infrared spectroscopy techniques. "The experiments pointed out to unexpectedly high levels of the enol form, and allowed us to go to the light source with well-focused questions," said Ghorai, a graduate student who began the study at EMSL in 2009.

At the Advanced Light Source at Lawrence Berkeley National Laboratory, they probed individual particles using scanning transmission X-ray microscopy combined with near-edge X-ray absorption fine structure spectroscopy.

"Dr. Tivanski and his colleagues took a novel approach to the synchrotron based X-ray microscope," said Dr. Mary Gilles, an expert in the X-ray spectro-microscopy and a beam line scientist at the Advanced Light Source at LBNL. "Most people use it in static mode, but they did dynamic studies -- watching as the particles chemically changed in relation to the relative humidity."

Combining the light source and EMSL resources allowed the researchers to see the malonic acid molecules at the molecular level and determine which form was dominant. "The complementary capabilities were perfectly leveraged," said Tivanski, a UI professor who led the project. "It would have taken endless time at the synchrotron to come to the same results and conclusion if the EMSL part had not been available."

With the results from EMSL and ALS, the team determined that the highly reactive enol form is 4 to 5 orders of magnitude higher in particles than would be predicted from aqueous chemistry. "The implications could be very broad," said Laskin, EMSL scientist. "If you have more reactive enol intermediates, then many chemical reactions are triggered that you didn't expect."

What's next: "We saw the behavior in one carboxylic acid. Will we see it in others? That's the question we are planning to explore in future studies," said Laskin. The team and others will determine the answers using and refining the new chemical imaging approach.

More information: Ghorai S, A Laskin, and AV Tivanski. 2011. "Spectroscopic Evidence of Keto-Enol Tautomerism in Deliquesced Malonic Acid Particles." *Journal of Physical Chemistry A* 115, 4373-4380. DOI: 10.1021/jp112360x

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