

Chemists map cascade of reactions for producing atmosphere's 'detergent'

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"Our detailed data proves a much sharper view of the actual dynamics of the troposphere," says theoretical chemist Joel Bowman. In this NASA photo of the space shuttle Endeavor, silhouetted against Earth's atmosphere, the troposphere is the orange layer. The white layer is the stratosphere and the blue is the mesosphere.

Chemists have identified a cascade of reactions for how mysterious molecules known as Criegee intermediates generate hydroxyl radicals – an oxidant that helps remove pollutants from the lower atmosphere.

Nature Chemistry is publishing the findings, a collaboration of Emory University and the University of Pennsylvania.

"We've solved another piece of the puzzle in the formation of [hydroxyl radicals](#), by zooming in to see all the steps of the reaction in much finer detail than ever before," says co-author Joel Bowman, a theoretical chemist at Emory. "This kind of detailed data is important to atmospheric chemists trying to make predictive models for how the atmosphere will respond to climate change."

The Bowman group collaborated with the lab of experimental chemist Marsha Lester at the University of Pennsylvania.

The theoretical work revealed that a Criegee intermediate first produces highly energized vinyl hydroperoxide, or VHP, then rapidly decomposes to hydroxyl radicals, along with vinyloxy byproducts.

In 2014, Lester's lab was the first to observe the creation of a hydroxyl radical by a Criegee intermediate in a laboratory setting. Many questions remained about the process, however, since it occurs so rapidly in the lab, as well as in the troposphere.

The turbulent troposphere, the lowest layer of Earth's atmosphere, is where the weather happens. It's like a giant washing machine filled with molecules – hydrogen, oxygen and nitrogen and all the other chemical byproducts of plant, animal and human activity that float up and mix with solar energy.

Hydroxyl radicals are sometimes called the detergent in this mix because

they are extremely reactive to many common pollutants and greenhouse gases. When a hydroxyl radical encounters a molecule of sulfur dioxide, for instance, it steals its electrons and oxidizes it. Both the hydroxyl radical and the [sulfur dioxide](#) vanish, turning into an innocuous aerosol.

Most hydroxyl radicals are produced during the daytime as sunlight breaks down ozone, releasing oxygen atoms that react with water vapor and become hydroxyl radicals. About a third of the troposphere's hydroxyl radicals, however, are produced through a more mysterious process that can even occur at night.



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German scientist Rudolf Criegee proposed a hypothesis in 1949 for this process. He predicted the existence of another radical, known as the Criegee intermediate, as a step in the chain of reactions needed to produce hydroxyl radicals from ozone, without daytime [solar energy](#).

"Alkene ozonolysis is a fancy term to describe the process Criegee proposed," Bowman says. "The Criegee intermediate, or carbonyl oxide, is one of the stepping stones in the process, but it has a lot of energy so it breaks up right after it forms. The Criegee intermediate was certainly possible – it followed the rules governing how bonds form and rearrange – but for decades it remained hypothetical."

It was not until 2012 that researchers managed to create a Criegee intermediate in a laboratory setting. That discovery was followed by the Lester lab's 2014 work: Actually tracking a Criegee intermediate through the reaction that results in a hydroxyl radical, using a technique known as infrared action spectroscopy.

For the current *Nature Chemistry* paper, the Lester lab teamed with the Bowman group to combine its experiments with theoretical modeling.

As theorists, the chemists in the Bowman group can slow down time, in a sense, to study and measure a reaction in more detail. "We have developed sophisticated algorithms and software codes that allow us to study chemical reactions at the ultimate level of detail," Bowman says. "Running the calculations for a reaction that occurs in picoseconds requires days of computer time, and we have to run it over and over again. The result is a mind-boggling data set, made up of billions of pieces, that we then have to analyze."

The theoretical results both extended the experimental work and were validated by them, giving an unprecedented insight into the multi-step cascade of reactions.

"What actually happens in the wild is so much more complicated than in a controlled laboratory setting," Bowman says. "Our detailed data provides a much sharper view of the actual dynamics of the troposphere."

Sophisticated experimental techniques, high-powered computers and powerful new algorithms are driving advances faster than ever before, he adds.

"A lot of science done prior to 50 years ago, before computers, involved brilliant people, like Rudolf Criegee, doing hypothetical work that they could not prove," Bowman says. "They would be bowled over by our capability now to actually settle many of these questions."

More information: Nathanael M. Kidwell et al. Unimolecular dissociation dynamics of vibrationally activated CH₃CHOO Criegee intermediates to OH radical products, *Nature Chemistry* (2016). [DOI: 10.1038/nchem.2488](https://doi.org/10.1038/nchem.2488)

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