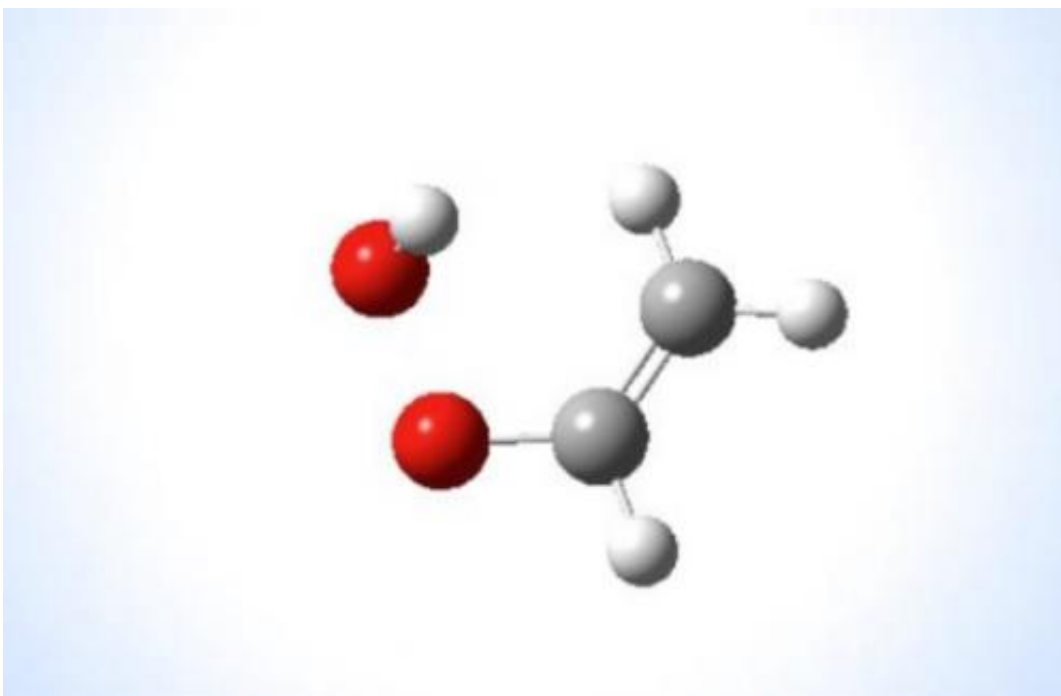


# Chemists observe key reaction for producing 'atmosphere's detergent'

September 26 2014, by Evan Lerner

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A hydroxyl radical (left) breaks away from the Criegee intermediate.

Earth's atmosphere is a complicated dance of molecules. The chemical output of plants, animals and human industry rise into the air and pair off in sequences of chemical reactions. Such processes help maintain the atmosphere's chemical balance; for example, some break down pollutants emitted from the burning of fossil fuels.

Understanding exactly how these reactions proceed is critical for

predicting how the atmosphere will respond to [environmental changes](#), but some of the steps of this dance are so quick that all of the molecules involved haven't been measured in the wild.

A University of Pennsylvania team has now observed one of these rapid atmospheric reactions in the lab. They identify an important intermediate molecule and track its transformation to [hydroxyl radicals](#), also demonstrating the amount of energy necessary for the reaction to take place.

Their findings help explain how the atmosphere maintains its reserves of hydroxyl radicals, highly reactive molecules that are called the "atmosphere's detergent."

The study was led by Marsha Lester, professor of chemistry in Penn's School of Arts & Sciences, along with members of her lab: graduate student Fang Liu and postdoctoral researcher Joseph Beames. They collaborated with Andrew Petit, also a postdoctoral researcher in the Department of Chemistry, and Anne McCoy, professor of chemistry at The Ohio State University.

Their work was published in *Science*.

Hydroxyl radicals are composed of a hydrogen atom bonded to an oxygen atom. They are highly reactive, readily stealing hydrogen atoms from other molecules to form water. Many common pollutants and greenhouse gases, such as methane and more complex hydrocarbons, are initially broken down by these radicals.

"Hydroxyl radicals are called the atmosphere's detergent because most pollutants that go into the air are broken down by them," Lester said. "Since they're so reactive, the question is then. 'How is it that there is so much of it in the atmosphere?' They're reacting away all of the time, so

they must be constantly replenished."

The sun is responsible for most of the hydroxyl radicals in the air in the daytime. Sunlight has sufficient energy to breakdown ozone, releasing oxygen atoms that react with water vapor to produce hydroxyl radicals. However, another important source of these molecules does not require sunlight. This less-well-understood process, investigated by the Lester team, is the dominant source of hydroxyl radicals at night, and plays a large role in the atmosphere during the winter.

In 1949, German chemist Rudolf Criegee hypothesized that alkenes, a class of chemicals with carbon double bonds, were broken down in reaction with ozone by way of intermediate molecules that were even more reactive and short-lived, so much so that they eluded detection until very recently. These intermediate molecules are now known as "Criegee intermediates."

Lester's team is now the first to track a Criegee intermediate through the reaction that results in a hydroxyl radical, using a technique known as infrared action spectroscopy.

"We used a laser to generate a 'fingerprint' of this intermediate molecule, based on the wavelengths of light it absorbs," Lester said. "The laser also supplies the energy necessary to drive the reaction, which would be provided by heat under atmospheric conditions."

"At the end," said Beames, "we also detected the hydroxyl radicals, so we're the first to actually show that the hydroxyl radicals are produced directly from the Criegee intermediate."

"We see that a hydrogen atom from one end of the intermediate molecule transfers over and bonds to an oxygen atom on the other side," said Liu. "The molecule then breaks apart, resulting in a hydroxyl

radical."

The team believes that the new understanding of the amount of energy necessary to drive this hydrogen transfer reaction will have implications for many of the hydroxyl-radical-producing reactions that involve Criegee intermediates.

"If you're going over a mountain—the energy it takes to drive the reaction—there are certain pathways it makes sense to follow," Petit said. "We're studying the simplest of this class of molecules so we think this pathway will be relevant to the others in the series."

A more complete picture of how the hydroxyl radicals are produced on an hour-to-hour and season-to-season basis will be instrumental to developing more accurate models of the atmosphere. Hydroxyl [radical](#) production through this route can also vary geographically, as the precursors to the reaction—alkenes—are more readily found above urban and forested regions.

"You can't measure everything," Lester said, "so we need good models to predict how the [atmosphere](#) will respond to changes in the environment, whether those changes are temperature, ozone levels or the presence of petrochemicals."

**More information:** "Infrared-driven unimolecular reaction of  $\text{CH}_3\text{CHO}$  Criegee intermediates to OH radical products." *Science* 26, September 2014: Vol. 345 no. 6204 pp. 1596-1598. [DOI: 10.1126/science.1257158](https://doi.org/10.1126/science.1257158)

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