

ALS

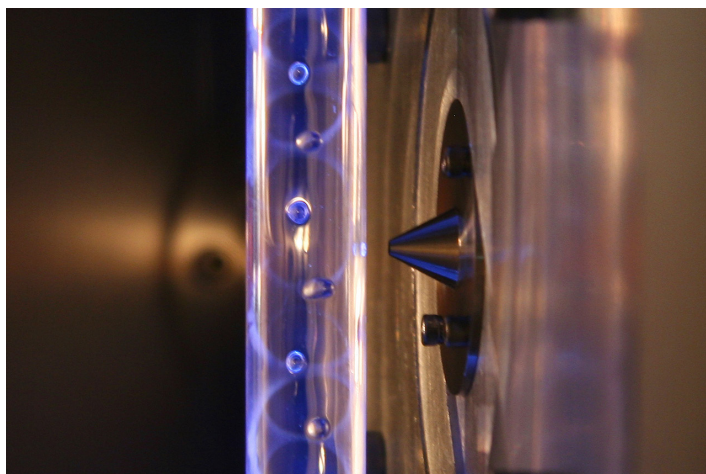
## SCIENCE HIGHLIGHT

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## Direct Kinetic Measurements of a Criegee Intermediate

In the Earth's troposphere, which blankets the planet surface where we live and breathe, dust particles, gas molecules, water vapor, and sunlight provide the ingredients for a multitude of chemical reactions that can generate effects ranging from clouds and smog to acid rain and climate change. In 1949, chemist Rudolf Criegee proposed a novel chemical pathway for one such reaction, known as ozonolysis: the destruction of alkenes (a type of hydrocarbon), via reaction with ozone, a key pollutant in the troposphere. Although there has been much indirect evidence supporting Criegee's mechanism, breakthrough research done at the ALS by chemists from Sandia National Laboratories, the University of Manchester, and Bristol University has for the first time directly measured reaction rates for so-called "Criegee intermediates," elusive molecules formed at intermediate stages of ozonolysis. The surprising results may have important implications for subjects ranging from advanced engine design to air quality and climate modeling.

The research was conducted primarily at the Chemical Dynamics Beamline (Beamline 9.0.2) of the ALS, where vacuum ultraviolet light from the ALS synchrotron is used to investigate chemical reactions that occur during critical



**The chemical reactions of Criegee intermediates were studied using an apparatus at ALS Beamline 9.0.2. A quartz reaction tube shows the faint blue luminescence from a 248-nm laser that creates a precursor reactant. A gas beam of the reactants and products exits the tube through a 600- $\mu\text{m}$  pinhole facing the conical skimmer on the right, which collects the molecules for eventual ionization by vacuum ultraviolet photons from the ALS and detection by a mass spectrometer. (Sandia photo by David Osborn)**

hydrocarbon oxidation processes (burning). Criegee intermediates—carbonyl oxides—are thought to play a key role in hydrocarbon autoignition chemistry, a field critical to advanced engine design. The detection of elusive Criegee intermediates is made possible by a unique apparatus designed by researchers from Sandia's Combustion Research Facility. In 2008, at Beamline 9.0.2, the research team made the first direct observation of a Criegee intermediate. In the current work, the Sandia researchers report a new, more intense source of gas-phase Criegee intermediates.

The process begins with the laser photolysis of  $\text{CH}_2\text{I}_2$  in a quartz reaction tube, generating the precursor reactant,  $\text{CH}_2\text{I}$ . The  $\text{CH}_2\text{I}$  reacts with a large excess of  $\text{O}_2$  to produce  $\text{CH}_2\text{OO}$ —formaldehyde oxide—the simplest form of Criegee intermediate. The intense tunable light from the ALS then allows the researchers to use time-resolved photoionization mass spectrometry to discern the formation of different isomeric species—molecules that contain the same atoms but are arranged in different geometrical configurations. Thus the short-lived  $\text{CH}_2\text{OO}$  produced in the reac-

Publication about this research: O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, C.J. Percival, D.E. Shallcross, and C.A. Taatjes, "Direct kinetic measurements of Criegee intermediate ( $\text{CH}_2\text{OO}$ ) formed by reaction of  $\text{CH}_2\text{I}$  with  $\text{O}_2$ ," *Science* **335**, 204 (2012).

Research conducted by: O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, and C.A. Taatjes (Sandia National Laboratories), C.J. Percival (University of Manchester, UK), and D.E. Shallcross (University of Bristol, UK).

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tion tube can be distinguished from its more stable isomers, such as formic acid ( $\text{HCOOH}$ ), by their differing thresholds for photoionization.

The Manchester and Bristol researchers recognized that the apparatus could elucidate not only combustion reactions but also important tropospheric oxidation processes, such as ozonolysis. Ozonolysis, or the cleavage of carbon-carbon double bonds through reaction with ozone, plays a key role in

## A Biradical Solution?

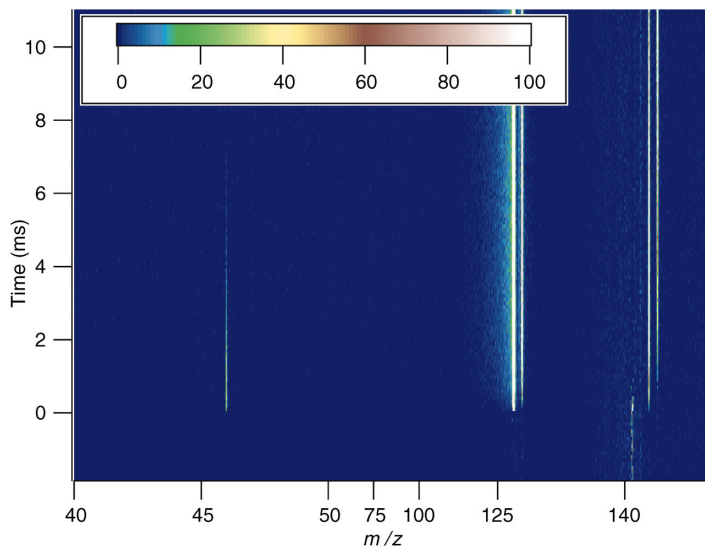
A biradical is a molecule with two unpaired electrons, each of which is a reactive site where a new bond can form with another molecule. As a result, biradicals such as Criegee intermediates are highly reactive and unstable, making them difficult to isolate and study, and impossible to produce and store in substantial quantities. Because Criegee intermediates have long been thought to play a key role in atmospheric chemistry, the announcement of a method to directly measure their reactivity has generated quite a bit of interest.

In this work, the researchers found that the simplest Criegee intermediate reacts up to 10,000 times faster with certain atmospheric molecules than previously thought. This doesn't change the actual chemistry occurring in Earth's atmosphere, but it might dramatically affect atmospheric chemistry models, portions of which we now know are incorrect. We are just beginning to understand the role Criegee species play: for example, although their reactions with  $\text{SO}_2$  can contribute to sulfate aerosols that act as cloud-condensation nuclei, tropospheric chemistry is too complex to know the full impact on climate models or other effects. Researchers will continue investigating how these natural biradicals operate in our atmosphere. "The ecosystem is negating climate change more efficiently than we thought it was," said co-author Carl Percival. "The most important message here is that we need to protect the ecosystems we have left."

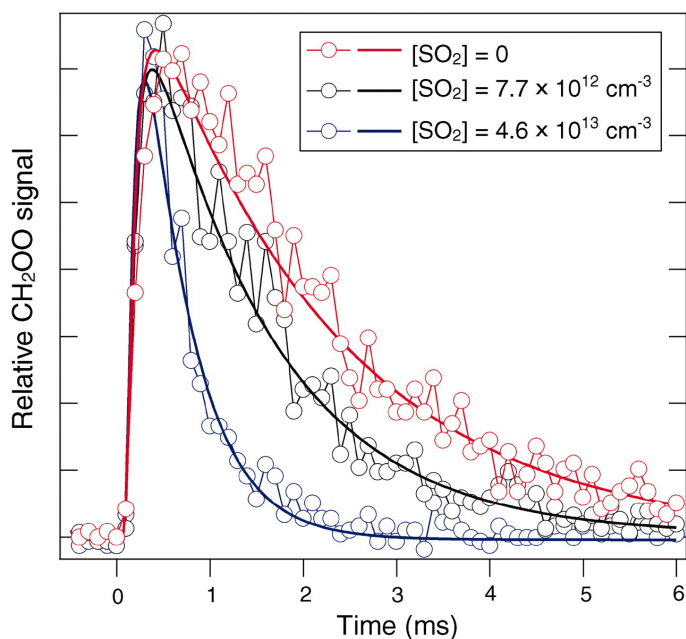
the removal of unsaturated hydrocarbons (alkenes) from the troposphere. Rudolf Criegee proposed that ozonolysis of alkenes occurs via carbonyl oxide biradicals, now called Criegee intermediates in his honor. However, the indirectly derived, earlier reaction-rate coefficients—which govern how large a role these species will play in the atmosphere—were inconsistent and spanned many orders of magnitude.

With the ability to generate and detect sufficient quantities of Criegee intermediates at Beamline 9.0.2, the research collaborators were able to determine the reaction-rate

coefficients of reactions with key species such as water,  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . In particular, the measurements show that the reactions of  $\text{CH}_2\text{OO}$  with  $\text{SO}_2$  and  $\text{NO}_2$  are much more rapid than previously thought—50 to 10,000 times larger than estimates typically used in tropospheric models. Moreover, the Bristol and Manchester investigators demonstrated that these kinetic results imply a much greater role for carbonyl oxides in tropospheric sulfate and nitrate chemistry than models had assumed, a conclusion that will substantially impact existing atmospheric chemistry mechanisms. The ability to



**Time-resolved mass spectrum at 10.5 eV showing the formation of  $\text{CH}_2\text{OO}$  at  $m/z$  (charge-to-mass ratio) = 46. The precursor reactant  $\text{CH}_2\text{I}$  ( $m/z = 141$ ) appears above a background from dissociative ionization of  $\text{CH}_2\text{I}_2$ . Other primary and secondary products (I, IO, HI, and HOI) are also evident.**



**Time-dependent  $\text{CH}_2\text{OO}$  signal for various concentrations of  $\text{SO}_2$ . Solid lines represent fits to the data traces. Analysis of the data gives reaction-rate coefficients that are 50 to 10,000 times larger than estimates typically used in tropospheric models.**

reliably produce Criegee intermediates will facilitate studies of their role in ignition and other oxidation processes as

well as enable new detection methods beyond photoionization that might be deployed for in situ atmospheric sensing.

