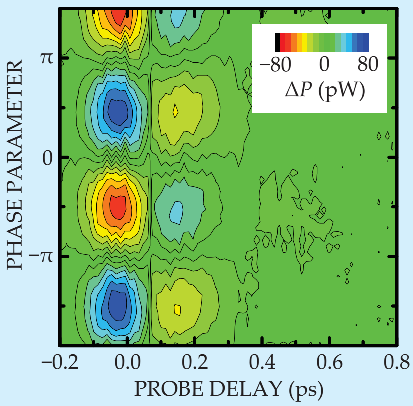

Figure 3. Current oscillations reveal themselves by the frequency-doubled light they induce. In this plot, the phase parameter, as described in the text, determines the initial amplitude and direction of the current. For a fixed phase, the current-induced power ΔP in frequency-doubled light oscillates as a function of time between current injection and second-harmonic generation. Both the lasers that inject current and the laser that triggers SHG have finite pulse widths. For that reason, current is observed even before the nominal injection time $t = 0$. (Adapted from ref. 5.)

oscillating plasma current, strongly damped because the charge flow occurs in a material medium. To measure it, Zhao and company observed the enhanced power in the frequency-doubled light, essentially just as they did in the DC case. In this more dynamic context, however, they did not map out current density as a function of position. Rather, they focused the interrogating laser beam on a fixed, 2.1-μm-diameter spot on the GaAs sample, but varied the time interval separating the injection of current by the pump lasers and the observation of SHG triggered by the interrogating laser. As figure 3 shows, the researchers observed a plasma oscillation period of about 0.4 ps (a half-cycle is readily apparent). Follow-up trials established that the oscillation amplitude depends on the angle between the current and the interrogating beam's polarization; it's greatest when the two are parallel. If the direction of current flow is unknown, one can determine it by finding the polarization that gives the maximum power in frequency-doubled light.

Admittedly, the separated electrons and holes affect the other charges in the GaAs, and so the sample is permeated with an electric field capable of inducing SHG. Intuitively, though, one might expect that the internal electric field would lag behind the inducing current. And indeed, experiments show the lag to be about a quarter period. The observed coincidence of current injection and maximum power in frequency-doubled light demonstrates that the SHG is induced by the current rather than by the field.

The 50-fs time resolution already achieved by his group, says Zhao, is superior to that of other current-measuring techniques and should enable studies of transient electron transport in graphene, carbon nanotubes, and other nanomaterials too small to support steady currents. Moreover, it can easily be improved with the help of shorter-pulsed lasers. Near-field optics may enable the team to improve its spatial resolution from 2 μm to about 100 nm. Even that superior resolution is not as good as could be obtained with, for example, electron microscopy. But current measurements via SHG and coherent current injection allow for the study of samples in situ. There's no need to alter them by attaching electrodes or to destroy them with high-energy electrons.

Steven K. Blau

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Criegee chemistry is captured

An elusive but atmospherically important molecule yields to kinetic measurement for the first time.

The chemistry of the atmosphere is complicated. Anthropogenic and naturally produced molecules undergo thousands of chemical reactions that affect urban pollution and smog, stratospheric ozone depletion, and global climate, among other things. Each reaction has its own kinetic rate constant, which must be known if the system is to be modeled and its effects understood.

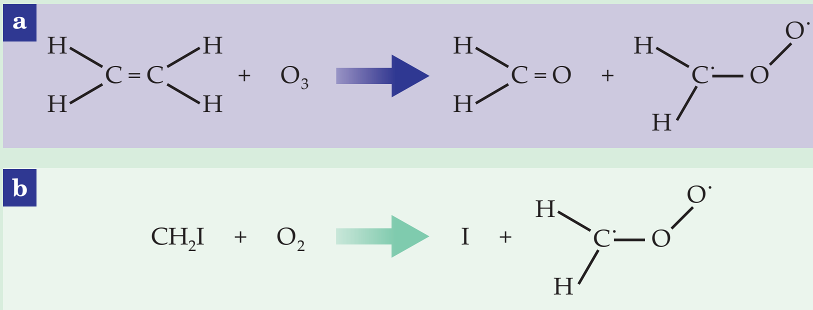

Figure 1. Cooking up Criegee intermediates. (a) In the atmosphere—and in many an organic chemistry lab—Criegee intermediates such as CH_2OO form by ozonolysis, the reaction of unsaturated hydrocarbons with ozone. **(b)** But the reaction of CH_2I with O_2 is more conducive to studying Criegee kinetics in the laboratory. The dots on the C and O atoms indicate unpaired electrons.

Among the key players in atmospheric chemistry is a class of unstable molecules called Criegee intermediates. Although qualitative evidence for their atmospheric role is strong, until recently no one had ever directly detected a Criegee intermediate in the gas phase, let alone measured its rates of reaction with other molecules.

Now, Craig Taatjes and David Osborn (both at Sandia National Laboratories in Livermore, California) and their colleagues have made several direct kinetic measurements on the reactions between the simplest Criegee intermediate, CH_2OO, and four small atmospheric molecules: SO_2, NO_2, NO, and water.[1] The results are particularly relevant to sulfate and nitrate chemistry in the atmosphere.

Mysterious molecules

As first suggested by Rudolf Criegee in 1949, the eponymous intermediates form during ozonolysis, the reaction of ozone (O_3) with alkenes, or unsaturated hydrocarbons. That reaction is shown in figure 1a. Alkenes and ozone are both abundant in polluted urban environments; so, too, are Criegee intermediates, which then react to form, for example, OH radicals, organic and inorganic acids, and low-volatility organic compounds that condense into aerosol droplets, or smog.

Ozonolysis has been well studied in the liquid phase, where it's an important tool in the synthetic organic chemistry toolbox. The final products are exactly what are expected, given the Criegee intermediates' involvement. Studies of ozonolysis products, and how those products change when other reagents are added to the mix, have allowed some estimates of the rates of Criegee reactions. Extracting reaction rates from final-product measurements requires extensive modeling of the whole reaction system, which is no easy task. But until now, it's all that atmospheric chemists have had to go on.

One challenge in making direct measurements has been in forming enough of the Criegee intermediate and keeping it around for long enough to measure it. For kinetic measurements, that means quantifying the rate of the CH_2OO decay and how that rate changes when other reactants are added. Another difficulty is in distinguishing the Criegee intermediate from similar-looking molecules. For example, the simplest Criegee intermediate, CH_2OO, is an isomer of formic acid, HCOOH, which is also an atmospherically important molecule.

Ah-CH_2OO

To overcome the first difficulty, the Sandia researchers created their CH_2OO not by ozonolysis but by reacting CH_2I with O_2, as shown in figure 1b. That reaction works well because it produces CH_2OO without too much destabilizing vibrational energy and because it doesn't produce any byproducts that react too quickly with the CH_2OO. Since CH_2I itself is not a stable molecule, they made it by exciting CH_2I_2 with a laser pulse, which breaks one of the carbon–iodine bonds and initiates the reaction.

Finding the right reaction to produce CH_2OO took a combination of trial, error, and inspiration. The researchers had already tried several less successful reactions when, in the spring of 2011, Arkke Eskola from the University of Helsinki in Finland gave a talk at Sandia about his work on the $CH_2I + O_2$ reaction that showed a near-100% yield of I atoms.[2] Taatjes and Osborn wondered what the other product might be. They found that it was CH_2OO.

To prove it—to distinguish CH_2OO from formic acid and other similar-looking molecules—the researchers used photoionization mass spectrometry. Mass spectrometry sorts a sample of ionized molecules by their mass (really their mass-to-charge ratio). When the ionization source is a beam of tunable, nearly monochromatic vacuum UV photons—available at the Advanced Light Source synchrotron at nearby Lawrence Berkeley National Laboratory—it's possible to distinguish between molecules with the same mass but different ionization potentials. The ionization potential of CH_2OO is 10.0 eV; of formic acid, 11.3 eV.

The Sandia researchers used an instrument Osborn had designed a few years before, which continuously records a mass spectrum of a reaction mixture as a function of time.[3] Figure 2 shows the time-resolved spectrum for the $CH_2I + O_2$ reaction for a photoionization energy of 10.5 eV. The Criegee intermediate forms rapidly and decays away within a few milliseconds. Adding another reagent, such as SO_2, to the mix shortened the CH_2OO lifetime. By varying the SO_2 concentration, the researchers extracted the reaction's rate constant.

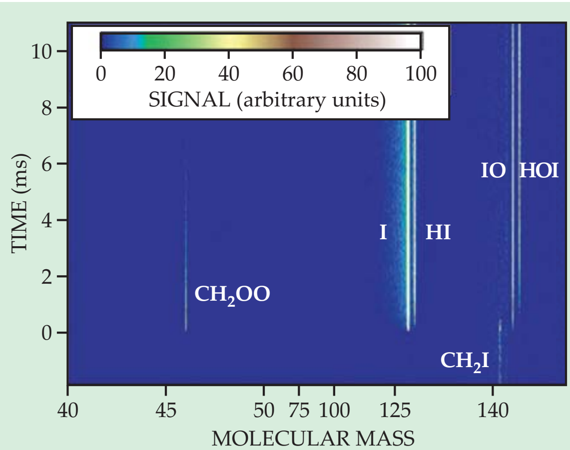

Figure 2. A time-resolved mass spectrum of the reaction in figure 1b. At time 0, a laser pulse initiates the reaction by dissociating CH_2I_2 to create CH_2I. (The CH_2I signal that appears before time 0 comes from CH_2I_2 molecules that break apart in the ionizer.) The Criegee intermediate CH_2OO appears at mass 46. Other primary and secondary reaction products appear at higher masses. (Adapted from ref. 1.)

Faster and slower

For three of the four reactions studied, the directly measured rate constants differed by orders of magnitude from the indirect estimates that had been derived from ozonolysis experiments. The reactions with SO_2 and NO_2 were much faster than expected, and the reaction with NO was much slower—in fact, there was no measurable reaction with NO at all. "Really, it seems like we were surprised by almost every aspect of the results," remarks Taatjes.

Collaborators Carl Percival (University of Manchester) and Dudley Shallcross (University of Bristol) analyzed some of the atmospheric implications. Among the products of the SO_2 and NO_2 reactions are SO_3 and NO_3. A rapid reaction between SO_3 and H_2O gives sulfuric acid, H_2SO_4, which contributes to atmospheric aerosol formation; NO_3 drives much of the chemistry of the atmosphere at night. Percival and Shallcross estimated that Criegee reactions could produce 40% as much NO_3, and more than 100% as much SO_3, as other known sources of those molecules.

They had to make some assumptions, though, since so far the Sandia team has studied only the smallest Criegee intermediate at only one temperature and pressure. Future experiments should clarify the picture.

Johanna Miller

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Microlensing suggests that our galaxy has more planets than stars

Gravitational bending of light reveals exoplanets with large orbital radii.

Most of the more than 600 exoplanets discovered to date have been found through Doppler evidence of periodic host-star motion or photometric evidence of transits across a star's face. Both methods are strongly biased in favor of planets with orbital radii much smaller than Earth's, which defines 1 astronomical unit (AU). Gravitational microlensing is an alternative technique that's most sensitive to planets a few AU from their stars. It favors very distant stars and it's relatively unbiased as to stellar mass. Though microlensing's discovery rate is still modest, it appeals to those who seek a representative galactic survey of planets with orbits like those of the solar system.

Gravitational bending of light is a central feature of general relativity. In a typical microlensing event, a foreground lensing star passing close by our line of sight to a background star produces milliarcsecond bending that focuses the background star so that it brightens over several weeks. Rarely, a planet several AU from the lensing star reveals itself by a short blip on the brightness curve as it too crosses the sight line (see the figure's panel a).

Because planetary blips typically last less than a day, finding and measuring them usually requires a two-tier strategy. First, a wide-field survey team, such as the OGLE collaboration based at the University of Warsaw, images the same star-crowded field night after night in search of the one in a million that's brightening. When the team finds one, it alerts one of several global networks of telescopes that then monitor the star round the clock for a telltale blip. If the blip is well measured, it yields the planet's mass M and orbital radius R. Since that strategy was initiated in the late 1990s, many thousands of stellar microlensing events have yielded only about two dozen planet sightings.

Now the PLANET telescope network, led by Jean-Philippe Beaulieu (Paris Institute of Astrophysics), reports an analysis of six years of its search for planets.[1] Translating planet sightings into an estimate of the galactic abundance and mass distribution of planets requires a careful determination of detection efficiency as a function of M and R. And that, in turn, requires adherence to a consistent, well-defined search protocol. So the PLANET analysis limits itself to the years 2002–07, after which innovations led to protocol modifications.

The only three planets discovered by PLANET during that period are plotted in panel b, together with eight discovered during the same period by other networks with protocols of their