

A mysterious player on the atmospheric stage

The unidentified molecule's reaction with sulfur dioxide has implications for climate and human health.

There's not much sulfuric acid in the atmosphere—its concentration is measured in parts per trillion—but it makes its presence known by condensing into aerosol particles. Near Earth's surface, the aerosols pose a hazard to human health; at higher altitudes, they attract water to form clouds, which affect both weather and climate. Atmospheric sulfuric acid forms when SO_2 is oxidized into SO_3 , which combines with water to make H_2SO_4 . The oxidation step is attributed to a reaction with OH radicals, highly reactive short-lived molecules that are formed by sunlight.

Now Lee Mauldin III (University of Helsinki and University of Colorado Boulder) and an international team of colleagues have shown¹ that there must be another atmospheric oxidant that, in some environments at least, can rival OH in its capacity for turning SO_2 into H_2SO_4 . The competing reactions are shown in panel a of the figure. The re-

searchers have built up a wealth of indirect evidence that the new oxidant is a Criegee intermediate, a type of unstable molecule that forms in a reaction between ozone and alkenes (unsaturated hydrocarbons), as shown in panel b. But in the absence of a direct measurement, they identify it only as "X."

The discovery was a product of work to measure atmospheric OH concentrations. A long-outstanding experimental challenge of atmospheric chemistry, OH measurements have been performed by only a handful of teams worldwide, including Mauldin's. The typical method is to combine an atmospheric sample with enough SO_2 that all the OH present reacts and forms H_2SO_4 .

To account for the possibility of other sources of H_2SO_4 , researchers repeat the measurement while adding to the sample not just SO_2 but also a scavenger compound that destroys OH radicals more quickly than they can react with

SO_2 . The difference in H_2SO_4 concentrations formed with and without the scavenger thus gives the OH concentration. As Mauldin recounts, "At first, we were more interested in getting the OH measurement right" than in uncovering the source of the background H_2SO_4 that formed in the presence of the OH scavenger. But as the OH data accumulated, it soon became clear that the background was often too strong to ignore.

The background exhibited some patterns. It correlated with ozone concentrations. And it was especially high in forested areas, where certain alkenes give evergreen trees their characteristic scents. Mauldin and colleagues took to the laboratory to check the correlations more precisely and found that they held: Add the necessary ingredients for a Criegee intermediate, and you oxidize more SO_2 .

That's strong evidence, but not proof, that the new oxidant X is a Criegee intermediate. Observing X directly, rather than via its reaction products, could close the case, but that would be a difficult measurement: Only in the past year was a gas-phase Criegee intermediate directly observed for the first time (see *PHYSICS TODAY*, March 2012, page 17). For now, the priority for Mauldin and colleagues is to work out the details of X's role in the atmosphere. Where and when is it most abundant? And other than SO_2 , what molecules if any does it react with?

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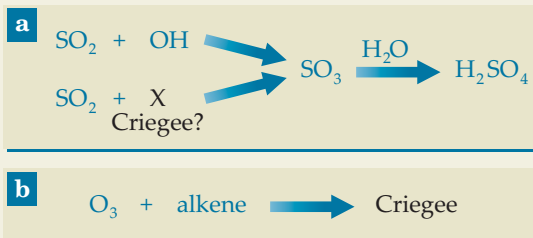
Reference

1. R. L. Mauldin III et al., *Nature* **488**, 193 (2012).

The conversion (a) of sulfur

dioxide to sulfuric acid is largely attributed to OH, which reacts with SO_2 in the presence of oxygen to form SO_3 . Lee Mauldin and colleagues have shown that there must be another molecule, which they identify as X and suggest may be a

Criegee intermediate, that does the same job. (b) Atmospheric Criegee intermediates form in a reaction between ozone and alkenes (unsaturated hydrocarbons).



physics update

These items, with supplementary material, first appeared at <http://www.physicstoday.org>.

Hearing chemical compounds in real time. The ability to detect and identify gaseous compounds quickly and accurately has many applications, whether for real-time pollution monitoring or for sensing chemical weapons on the battlefield. A common, sensitive method for measuring a trace gas is laser photoacoustic spectroscopy. In LPAS, the absorption of laser light by a sample generates local heating, which in turn generates acoustic waves; those waves can be detected by a sensitive microphone and analyzed (see *PHYSICS TODAY*, May 2009, page 34). Now Kristan Gurton and colleagues at the Army Research Laboratory have demonstrated a way to expand LPAS to multiple absorption signals, which allows the presence of a particular gas species to be detected in real time. The team's approach is facilitated by the increased availability of lasers—particularly quantum cascade lasers—in the spectrally rich mid-IR. The researchers filled a photoacoustic cell with the gas to be analyzed and then

illuminated it with three lasers of different wavelengths simultaneously. By modulating each laser at a different frequency, Gurton and company could separate out from the microphone signal the absorption at each laser wavelength; the ratios of the absorption signals yielded concentration-independent metrics. Tests on varying concentrations of different compounds—acetone, isopropyl alcohol, and five chemical nerve agents—exhibited clear absorption-ratio distinctions for all but two of the species, as seen here, with parts-per-million sensitivity. Adding additional lasers at different wavelengths should allow greater discrimination. The researchers envision that a sufficiently rugged device for field use would be about the size of a milk carton. (K. P. Gurton, M. Felton, R. Tober, *Opt. Lett.* **37**, 3474, 2012.)

—RJF

