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AEROSOL ARCHITECT

A new flow reactor in Finlayson-Pitts's lab can be used to study aerosols under various conditions and reaction times.

The nucleation of aerosol particles from gaseous components in the atmosphere has been a particularly tricky area to study. Researchers have long known particle nucleation to be strongly dependent on the atmospheric concentration of sulfuric acid, which is formed from the oxidation of sulfur dioxide emissions. One possible nucleation scenario is that sulfuric acid and perhaps one or more “sticky” organic molecules—the necessity of other species is much debated—collide in the air, says James N. Smith, a chemist at the National Center for Atmospheric Research (NCAR), in Boulder, Colo. If two molecules stay together long enough to encounter a third, they might form a thermodynamically stable cluster that can continue to collide with other molecules and build up mass. The critical size, Smith says, is about 1 nm in diameter. “It’s at that point that we say nucleation has taken place,” Smith says.

“But it’s a very difficult size to observe in the atmosphere,” Smith adds. Most of the clusters are neutral in charge and hard to identify. Condensation particle counters, the traditional instrumentation for measuring particles by light scattering can detect down to about 3 nm. Although finding a 3-nm particle “definitely implies that a nucleation event preceded it,” Smith says, the absence of particles does not necessarily mean that nucleation did not occur. Before freshly nucleated particles grow large enough to be detected, they could, for example, get stuck on the walls of the reaction chamber. NCAR scientists have been working with University of Minnesota mechanical engineering professor Peter H. McMurry to develop ultrafine-particle counters to look directly for 1–2-nm particles, along with a mass spectrometry technique to measure clusters with molecular masses of 50 to 900 amu.

Using similar techniques, Markku Kulmala, a physics professor and the director of the division of atmospheric sciences in the department of physical sciences at the Uni-

ASSESSING AEROSOLS IN THE AIR

Researchers delve into the unknowns of **AIRBORNE PARTICULATES** that affect health and climate

JYLLIAN KEMSLEY, C&EN WEST COAST NEWS BUREAU

WHEN IT COMES TO the quality of Earth’s atmosphere and the overall temperature of the globe, much of the discussion focuses on carbon dioxide and other greenhouse gases, such as methane and nitrous oxide. But another component of the atmosphere, suspended particles known as organic aerosols, plays a similarly important role.

Ranging in size from 1 nm to tens of micrometers, aerosols can be directly emitted as so-called primary aerosols from industrial processes, biomass burning, volcanic emissions, or sea spray. Alternatively, they can nucleate from gaseous chemicals in the atmosphere, in which case they’re called secondary aerosols. Aerosol particles typically contain a mixture of components in solid or liquid form. Those components include sulfate, nitrate, and ammonium salts; organic compounds; graphitic or “black” carbon from combustion; water; and trace metals. Aerosols from marine environments

also incorporate sodium and chloride.

Aerosols pose a host of human-health concerns—they are respiratory irritants, can cause cardiovascular problems, and are linked to increased mortality. In terms of climate, they can absorb or scatter sunlight, depending on their chemical composition. If the particles are or grow large enough, they can also seed clouds, which further reflect light and play a major role in determining global temperatures and precipitation.

Yet, despite aerosols’ importance for health and climate, aerosol chemistry—particularly the ways in which new particles form and are chemically processed in the air—is poorly understood. Atmospheric scientists are working to increase understanding of the particles through a combination of atmospheric observation and laboratory experimentation, with the ultimate goal of improving air quality and climate modeling.

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iversity of Helsinki, in Finland, has detected particles down to about 1.5 nm (*Science* 2010, 327, 1243). Kulmala and colleagues give the particles about 115 seconds to nucleate and grow in a laminar-flow tube before counting. They found that they could reproduce atmospheric observations in terms of H_2SO_4 concentration and number of particles formed without the need for other chemical species. But Kulmala notes that other species may still play a role in nucleation mechanisms, depending on geographic location and atmospheric composition.



JOHN SEINFELD/CALTECH

Once aerosols have formed in the atmosphere, they can grow by scavenging other small particles, as well as by accumulating additional chemicals from the air. In addition, the particles are subject to chemical processing. Both inorganic and organic compounds play a role as the particles grow to 100 nm—the minimum size required to spur cloud formation—over a period of as long as a week.

BRIGHT IDEA The Teflon reaction chambers in Seinfeld's lab are surrounded by ultraviolet lights to stimulate photochemistry.

Researchers such as John H. Seinfeld, a chemical engineering professor at California Institute of Technology, are investigating some of the atmospheric chemicals that likely play a role in the growth and aging of aerosols. "The process involves the formation of oxidized, low-volatility

organic compounds that will condense and partition between gas and particle phases," Seinfeld says.

"We've studied probably close to 100 different compounds over the years, ranging from isoprene, which is the second most abundant hydrocarbon in the atmosphere after methane, all the way to terpenes, sesquiterpenes, and aromatic compounds," Seinfeld adds. "The more we look, the more compounds we find" that play a role in aerosol growth.

FOR EXAMPLE, recent work by Seinfeld, Caltech environmental science and engineering professor Paul O. Wennberg, and colleagues suggests aerosols likely take up oxidized forms of isoprene, or 2-methyl-1,3-butadiene (*Science* 2009, 325, 730; C&EN, Aug. 10, 2009, page 10). Emitted by deciduous plants, isoprene reacts with HO^* to form primarily hydroxyhydroperoxides, which further react with more HO^* to form dihydroxyepoxides. Acidic aerosol seeds formed from $MgSO_4$ and H_2SO_4 readily take up a similar epoxide, the researchers found.

Even smaller hydrocarbons can play a

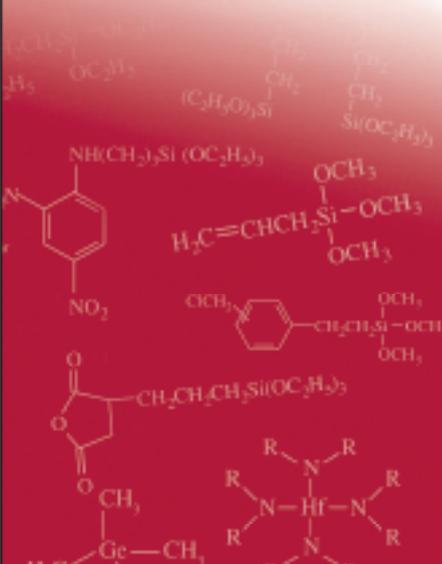
role in aerosol growth. Glyoxal, $OCHCHO$, and methylglyoxal, CH_3COCHO , are formed in the atmosphere from gas-phase oxidation of a variety of biogenic and anthropogenic compounds, says V. Faye McNeill, a chemical engineering professor at Columbia University. The two "are examples of molecules that can be absorbed into an aerosol particle and undergo aqueous-phase oligomerization chemistry to add organic material," McNeill says.

Experimental work in McNeill's lab has shown that when methylglyoxal or glyoxal are mixed with ammonium nitrate or ammonium sulfate in aqueous solutions that mimic liquid components of aerosol particles, the organic compounds form aldol condensation products and other oligomeric compounds with molecular masses up to 759 amu, along with some nitrogen- and sulfur-containing species (*Atmos. Chem. Phys.* 2010, 10, 997).

McNeill also notes that the organic compounds formed from glyoxal or methylglyoxal absorb ultraviolet light and could therefore change the optical properties of aerosol particles. Increasing the ability of



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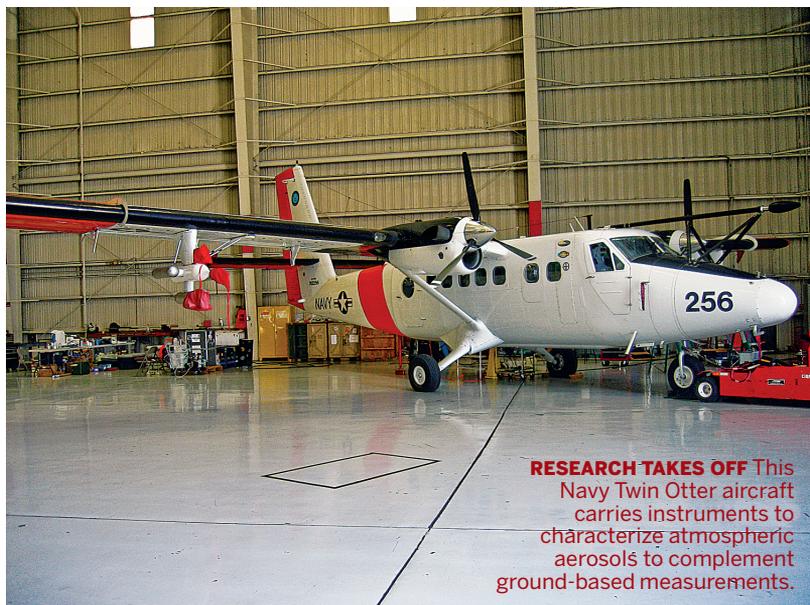
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particles to absorb light could affect not just temperature but also atmospheric photochemistry, such as the formation of air-scrubbing HO^{*} from peroxide or ozone reactions.

For his part, NCAR's Smith, in collaboration with Helsinki's Kulmala and Minnesota's McMurry, has been investigating how the incorporation of protonated amines could affect aerosols. "Amines coupled with organic acids are probably one of the mechanisms by which very volatile gases in the atmosphere, once combined, turn each other into an ion," Smith says. "And once something is an ion, it has no reason to leave the solid phase," thereby ensuring that once protonated amines are deposited onto a particle, they stay put.

Using MS, Smith's team has probed the aerosols in the air above the urban area of Tecamac, Mexico, for protonated amines. Aminium cations (R₃NH⁺, in which the R groups can be H or alkyl groups from organic acids) accounted for about 60% of the positive ions detected in aerosols (*Proc. Natl. Acad. Sci. USA* 2010, 107, 6634). Above the remote forests in Hyttiälä, Finland, the number was 23%. "These organic salts dominate the growth" of aerosol particles, McMurry says, yet current atmospheric models don't account for them. A better understanding of the processes involved would improve models of aerosol growth and climate effects, he says.

As aerosols continue to grow and age, their components become progressively more oxidized until there's nearly a 1:1 ratio of oxygen to carbon atoms (*Science* 2009, 326, 1525). Neil M. Donahue, a chemistry and chemical engineering professor at Carnegie Mellon University, describes the process as "a sophomore synthetic chemistry lab gone wrong," akin to when a student winds up with nothing but "brownish goo" in the bottom of a test tube. "As far as we can tell, there's a whole mess of different molecules" in that goo, but teasing out the carbon number and molecular weight of individual molecules is difficult with current analytical methods, he says. Donahue adds that regardless of where a particle originated



RESEARCH TAKES OFF This Navy Twin Otter aircraft carries instruments to characterize atmospheric aerosols to complement ground-based measurements.

JYLLIAN KEMSLEY/C&EN

their ability to nucleate clouds. As aerosols age and their components become more oxidized, bulk chemical analyses indicate that there are lots of hydrophilic polar groups, "but they're not necessarily on the surface," Finlayson-Pitts says.

Work in her lab aims to mimic the ozonolysis of surface-bound alkenes, modeled as self-assembled monolayers on a silica substrate (*Atmos. Environ.* 2010, 44, 939). Analysis of the

and the chemicals to which it might have been exposed, the oxidation that aerosols undergo means that "they all wind up with similar-looking goo."

Meanwhile, other researchers are investigating the role aerosols play in processing atmospheric emissions such as NO and NO₂, which react to give N₂O₅ in air. It's thought that the hydrolysis of N₂O₅ "may be responsible for removing 30–50% of the nitrogen oxides emitted into the atmosphere, and it only happens in a condensed phase"—that is, on an aerosol particle, says Joel A. Thornton, a professor of atmospheric sciences at the University of Washington. And because the production of ozone—a harmful pollutant and greenhouse gas in the lower atmosphere, but one that filters ultraviolet light in the upper atmosphere—depends on the availability of nitrogen oxides, an accurate picture of N₂O₅ chemistry is necessary for climate modeling.

Thornton is using MS in field studies to try to understand N₂O₅ reactivity in the atmosphere. Data collected in Boulder, Colo., and Seattle indicate that the rate of the reaction of N₂O₅ with aerosol particles depends on the relative humidity and the ratio of organic matter to sulfate in the particles (*Geophys. Res. Lett.* 2009, 36, L19803). The reaction rate is also more variable and as much as 10 times lower than current atmospheric models predict.

For her part, Barbara Finlayson-Pitts, a chemistry professor and director of the Atmospheric Integrated Research Using Chemistry at Interfaces Institute at the University of California, Irvine, is focusing on the surfaces of aerosols, which are key to the particles' hygroscopicity and

monolayers using infrared spectroscopy and MS showed that the reactions form carboxylic acid and other polar groups, but they wind up buried inside a hydrophobic shell. If the same thing happens on aerosols in the atmosphere, the particles would then take up less water than expected given their overall chemical composition. A hydrophobic surface shell could also play a role in the uptake of aerosols by biological surfaces such as in the lungs. The results, Finlayson-Pitts says, point to a need to develop analytical methods that allow researchers to "peel a particle like an onion" and get a better idea of its three-dimensional chemical composition.

EVEN AS RESEARCHERS are starting to unravel some of the details of the formation, growth, and chemical processing of secondary organic aerosols, much is still left to understand. Although particles probably contain similar inorganic salts and organic compounds, the proportions of the components likely vary from particle to particle or population to population. Researchers also don't know whether the particles are largely solid or liquid, or whether the solid parts are crystalline or amorphous. Another question is whether reactions occur in the gas phase, in the aerosol bulk, or at the interface between the two. All of these factors likely play into the chemistry that can and does occur and the rate at which it occurs.

"There's a lot more that we don't know than we do know," Finlayson-Pitts says. Understanding these details will be critical for a better understanding of atmospheric chemistry, along with improving long-term climate modeling. ■