

Esselen Award Address

Atmospheric Ozonolysis: From Collisional Energy Transfer to Particle Physics and Everything in Between

By Neil M. Donahue



Particle number and particle mass sit at the center of two pressing topics in atmospheric chemistry: air pollution and climate change. Fine-particle air pollution kills more than 3.5 million people each year, roughly 50,000 of them in the United States. Aerosol climate forcing masks roughly one third of the warming locked in by long-lived greenhouse gases, but the factor could be as much as half or as little as nothing. As the global economy decarbonizes, in part motivated by the parallel desire to clean up extremely polluted air in developing cities, it is likely that much of that masking will be erased, revealing the hidden warming over and above the degree or so already realized from human activity.

Most of the particles influencing climate and health are between 100 and 1000 nm in diameter. 100-nm particles contain roughly 1 million molecules, while 1000-nm particles contain 1 billion molecules. Health effects appear to depend largely on the total mass and composition of the particles (the dosage) while the climate effects depend both on surface area (direct Mie scattering by particles with sizes comparable to the wavelength of visible light) and the number of particles large enough to serve as cloud condensation nuclei, or CCN (driven by particle swelling and Raoult's law suppression of water vapor pressure over forming cloud droplets). We thus seek to understand both the total number and total mass of fine particles.

More than half of the mass of most fine particles over much of the globe consists of a vast array of organic compounds, and the large majority of those compounds are formed in the atmosphere by a combination of oxidation chemistry and condensed-phase association reactions. Furthermore, almost all particles larger than 100 nm start much

smaller – at 10s of nm for primary (emitted) particles and as 1 nm molecular clusters for nucleated particles. Small particles have high Brownian diffusivity and so must grow rapidly or else die via collisions with larger particles. For all of these reasons we are interested in the contribution of gas-phase organic oxidation to new-particle formation and particle growth.

To stick to a particle, organic molecules require a vapor pressure less than roughly 10^{-10} atm, an exceptionally low value characteristic of paraffin wax or even monosaccharides. To nucleate a particle, even lower vapor pressures (with high saturation ratios) are required. Thus, how gas-phase oxidation chemistry generates extremely low volatility organics is a question that has defined much of our research over the past decade.

Many volatile precursors are unsaturated – especially the terpenoids emitted from vegetation, including isoprene, monoterpenes, and sesquiterpenes. These unsaturated organics can be oxidized by ozone via ozonolysis, and the ozonolysis mechanism is the first of two vignettes we will cover. Gas-phase ozonolysis is extremely exothermic, releasing more than 50 kcal/mole when ozone bridges the double bond of an alkene to form a primary ozonide (1,2,3-trioxolane), which in turn rapidly decomposes to form a carbonyl (ketone or aldehyde depending on the substitution of the double bond) and a carbonyl oxide (Criegee Intermediate). For linear alkenes the excess reaction energy is spread between the carbonyl and carbonyl-oxide products and also external modes, while for endocyclic alkenes (such as α -pinene) the carbonyl and carbonyl-oxide moieties remain on a single product retaining all of the reaction energy. One possible fate of the carbonyl oxides is to decompose, to making radicals including OH, while another is to be collisionally stabilized, forming highly reactive stabilized Criegee Intermediates. Starting with Laser Induced Fluorescence measurements of OH formation vs pressure at Harvard in the late 1990s, we have studied the influence of alkene structure and pressure on this system. A major interest now is the yields and subsequent fate of stabilized Criegee Intermediates. They can oxidize SO_2 and under some circumstances can be a major source of gas-phase H_2SO_4 , which in turn is a crucial precursor for atmospheric new-particle formation.

Recently, we have used the reaction of stabilized Criegee Intermediates with SO_2 as a probe of the stabilization yield. Specifically, because OH radicals produced from ozonolysis also oxidize SO_2 to H_2SO_4 , we use highly sensitive nitrate ion chemical ionization to detect H_2SO_4 formed in a flowtube containing ozone, an alkene, and SO_2 , with and without a scavenger that selectively removes OH radicals. We operate the flowtube at pressures ranging from 30 torr to 1000 torr and measure the pressure dependence of Criegee Intermediate stabilization. We have applied this to a canonical

system – tetramethyl ethylene, as well as a sequence of symmetrical trans alkenes and a sequence of monoterpenes.

We observe stabilization at progressively lower pressures for increasing carbon number in the linear trans alkenes, consistent with theoretical expectations. For trans-5-decene and trans-7-tetradecene stabilization is essentially complete below 760 torr. However, to quantitatively analyze the stabilization yield we need to know the branching ratio between two excited carbonyl oxide conformers as a function of pressure. For syn carbonyl oxides the terminal O faces an R group on the COO moiety whereas for anti carbonyl oxides the terminal O faces an H atom. The OH yields are very different, near unity for syn and near 15% for anti, as Jesse Kroll established during his doctoral research at Harvard. Though the unimolecular barrier for anti carbonyl oxide isomerization to dioxyrane (a CO- O ring closure) is lower than the uni-molecular barrier for syn carbonyl oxide isomerization to a vinyl hydroperoxide (an H-atom transfer), tunneling may lower the effective activation energy for the second process, resulting in more effective collisional stabilization for the anti carbonyl oxides.

Experiments in Marsha Lester's group at the University of Pennsylvania have recently demonstrated that tunneling is highly efficient for H-atom transfer from acetone oxide, which can be synthesized without excess vibrational energy. In a collaboration, we have combined our pressure-dependent data from tetramethyl ethylene ozonolysis (which produces acetone and acetone oxide), the Lester group state-resolved rate measurements, and quantum-chemical calculations of the reaction co-ordinate in a master-equation simulation of the system. The results are self-consistent, explaining both the pressure dependence and low-energy unimolecular rate data.

Our measurements of carbonyl oxide stabilization for terpenes show small but non-negligible stabilization for exocyclic terpenes such as β -pinene and endocyclic terpenes such as α -pinene. This production of both syn and anti stabilized carbonyl oxides may be sufficient to explain high residual conversion of SO₂ to H₂SO₄ observed in boreal-forest measurements originally designed to measure OH radicals. However, the large majority of carbonyl oxides produced in terpene ozonolysis will isomerize in the atmosphere without collisional stabilization, and the resulting organic radicals will undergo further reactions to produce reaction products that may be involved in new-particle formation and growth. That process constitutes our second vignette.

Atmospheric new-particle formation is responsible for more than half of the particles that serve as CCN in the present-day atmosphere, and may have been the source of a far greater fraction in the pre-industrial. Uncertainty in the CCN number, especially for the pre-industrial, is one of the largest sources of uncertainty in our overall estimation of

climate forcing. The problem is challenging because aerosol-cloud interactions (the “indirect” effect of particles on climate) are especially sensitive to when CCN concentrations are small because cloud-droplet properties change significantly, whereas the effect saturates at higher concentrations. Thus, if pre-industrial CCN levels were high, increased CCN from anthropogenic pollution will not have had much negative climate forcing (cooling), whereas if pre-industrial CCN levels were low, pollution may have had a dramatic cooling effect and masked up to half of the total warming from long-lived greenhouse gases.

In the Cosmics Leaving Outdoor Droplets (CLOUD) experiment at CERN, we seek to conduct experiments under tightly controlled conditions spanning the conditions of temperature, reagent and oxidant concentrations and ion-pair formation rates found in the present-day and the pre-industrial atmosphere in order to isolate the molecular interactions responsible for atmospheric new-particle formation. A key feature of CLOUD experiments is an array of state-of-the-art particle sizing instrumentation complemented by a suite of mass spectrometers to measure the composition of both condensible vapors and the growing particles. Extraordinary advances in mass spectrometer resolution and sensitivity over the past decade, many driven by Doug Worsnop and his team at Aerodyne Research, have revealed surprises at almost every turn.

Nucleation often involves a mixture of inorganic (sulfuric acid and bases) and highly oxidized organic compounds, with different mixtures typifying different regions (location and altitude) of the atmosphere. In a series of campaigns, we have studied the ozonolysis of α -pinene over a wide temperature range, with and without sulfuric acid and with and without ion clusters. We observe nucleation under all conditions at rates consistent with ambient observations, showing that purely organic particles can form and that particles involving clusters of organics and sulfuric acid can form at higher rates given sufficient sulfuric acid (typical of the present day). Particle growth rates accelerate between 1 and 10 nm, indicating a strong “Kelvin” effect in which vapors evaporate rapidly from highly curved tiny particles, but condense to larger particles; we can explain this quantitatively, and the implications for particle survival probabilities are significant.

A fascinating and relatively exotic combination of minor but important oxidation pathways dominates new-particle formation associated with oxidation of α -pinene and other organic compounds. The key players are organoperoxy radicals, some of which engage in rapid “auto-oxidation” reactions within seconds to produce highly oxidized products in a single generation (defined as progression from a long-lived precursor to a long-lived product compound). Some highly-oxidized peroxy radicals combine with each other to produce covalently bound products which, by dint of their large number of polar

functional groups and large carbon number, have a sufficiently high gas-phase supersaturation to overcome the free energy barrier to nucleation. Some more volatile species condense to growing particles and react to form less volatile association products, increasing growth rates. The reactions, nucleation rates, and subsequent growth rates depend sensibly on temperature, revealing a mechanism that may have dominated new-particle formation during the pre-industrial epoch.