Abstract

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

Atmospheric new-particle formation is responsible for more than half of the particles that serve as Cloud Condensation Nuclei (CCN) in the present-day atmosphere, and may have been the source of a far greater fraction in the pre-industrial era. Uncertainty in the CCN number, especially for the pre-industrial era, is one of the largest sources of uncertainty in our overall estimation of climate forcing. The problem is vexing because aerosol-cloud interactions (the “indirect” effect of particles on climate) are especially sensitive to when CCN concentrations are small because clouddroplet 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 longlived 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. Nucleation often involves a mixture of inorganic (sulfuric acid and bases) and organic (highly oxidized) compounds, with different mixtures typifying different regions (location and altitude) of the atmosphere. Recently we have found that a fascinating and relatively exotic combination of minor but important oxidation pathways dominates new-particle formation associated with 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. The reactions, nucleation rates, and subsequent growth rates depend sensibly on temperature, revealing a mechanism that may have dominated new-particle formation during the preindustrial epoch.