Formation of nanoparticles of blue haze enhanced by anthropogenic pollution

Renyi Zhanga,1, Lin Wanga, Alexei F. Khalizovb, Jun Zhaoc, Jun Zhenga, Robert L. McGrawb, and Luisa T. Molinac,cd

aDepartment of Atmospheric Sciences and Department of Chemistry, Texas A&M University, College Station, TX 77843; bAtmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY 11973-5000; cMolina Center for Energy and the Environment, La Jolla, CA 92093; and dMassachusetts Institute of Technology, Cambridge, MA 02139

Communicated by Mario J. Molina, University of California at San Diego, La Jolla, CA, September 3, 2009 (received for review May 4, 2009)

The molecular processes leading to formation of nanoparticles of blue haze over forested areas are highly complex and not fully understood. We show that the interaction between biogenic organic acids and sulfuric acid enhances nucleation and initial growth of those nanoparticles. With one cis-pinonic acid and three to five sulfuric acid molecules in the critical nucleus, the hydrophobic organic acid part enhances the stability and growth on the hydrophilic sulfuric acid counterpart. Dimers or heterodimers of biogenic organic acids alone are unfavorable for new particle formation and growth because of their hydrophobicity. Condensation of low-volatility organic acids is hindered on nano-sized particles, whereas ammonia contributes negligibly to particle growth in the size range of 3–30 nm. The results suggest that initial growth from the critical nucleus to the detectable size of 2–3 nm most likely occurs by condensation of sulfuric acid and water, implying that anthropogenic sulfur emissions (mainly from power plants) strongly influence formation of terrestrial biogenic particles and exert larger direct and indirect climate forcing than previously recognized.

aerosol | biogenic | climate | nucleation | forest

Forests emit an enormous amount of nonmethane hydrocarbons, such as monoterpenes that have a global emission rate on the order of 1014 g yr−1 (1). The α- and β-pinenes are the two most abundant monoterpenes in the troposphere, accounting for ≈60% of the total terpene budget. Went (2) first recognized the phenomenon of blue haze over forests, and attributed its formation to biogenic plant emissions. The monoterpenes react with atmospheric oxidants to form a number of products (3, 4), some of which undergo gas-to-particle conversion to form secondary aerosols. Aerosols formed over forested areas contribute importantly to the global aerosol burden, and impact the climate directly by scattering incoming solar radiation, indirectly by altering cloud formation as cloud-condensation nuclei (CCN), or by being involved in multiphase atmospheric chemical processes (5–7).

Biogenic hydrocarbons likely promote secondary aerosol formation in several distinct ways. Photochemical oxidation of biogenic hydrocarbons leads to formation of low-volatility products that likely contribute to particle nucleation. For example, pinonic acids have been suggested as important products from α-pinene reaction with ozone (8). Field measurements indicated that pinonic acids represent an important constituent of nano-sized particles over forests (9). Also, oxygenated organic species, which are formed from oxidation of biogenic hydrocarbons (10–12), may engage in heterogeneous reactions to lead to aerosol growth (13–15).

Several mechanisms have been proposed to explain nucleation events in the continental troposphere, including binary H2SO4/H2O and ternary H2SO4/H2O/NH3 nucleation (16), ion-induced nucleation (17, 18), and nucleation enhanced by aromatic organic acids (19). Sulfuric acid has been widely identified as a major atmospheric nucleating species (20, 21). New particle formation is kinetically limited by the population of critical nuclei (22), but little is known about the chemical compositions of the critical nuclei and the identity of other species that also participate in nucleation. Another area of major uncertainty in new particle formation is the mechanism of the initial growth from the critical nucleus to the detectable size of 2–3 nm. Compounds that have been suggested as the likely candidates for nano-sized particle growth include ammonia and organics, in addition to sulfuric acid (22).

Results and Discussion

We conducted experimental and theoretical studies to investigate nucleation and initial growth of nano-sized biogenic aerosols over forests. Biogenic organic acids including cis-pinonic acid (CPA) and their mixtures with sulfuric acid and water were used as a model system to mimic nucleation of biogenic particles (23) in an aerosol chamber. Aerosols (>2 nm) were generated when gaseous H2SO4 was delivered into the nucleation chamber along with a humidified nitrogen carrier gas, and the particle size and distribution were determined by using a nano-differential mobility analyzer (DMA). A pronounced increase in new particle formation over the H2O/H2SO4 binary system occurred when CPA was introduced at a concentration on the order of 10−10−109 molecule cm−3. Fig. 1A shows that the measured particle size ranges from 2 to 4 nm, with a variable peak size depending primarily on the H2SO4 concentration. The nucleation rate increased with CPA and H2SO4 concentrations (Fig. 1 B–E).

In the absence of sulfuric acid, no new particle formation occurred, even when the concentration of CPA reached a value of 20–30 times higher than its saturation concentration of ≈1.7 × 1010 molecule cm−3 at room temperature. Additional experiments were performed to survey new particle formation with the coexistence of two different organic acids, including pinic and norpinic acids that are also coproducts of α-pinene ozonolysis (8). A previous environmental chamber study suggested that organic aerosol nucleation might occur through formation of stable organic heterodimers (24). On the basis of analysis of the molecular composition of particle-phase ozonolysis products of α-pinene, the formation of difunctional carboxylic acids was shown to govern most of the mass in the particle-phase. A strong intermolecular force between different diacids was suggested to play a key role in the formation of initial nuclei and their subsequent growth. We did not detect new particle formation using a combination of two of the three organic acids with the concentrations of the organic acids as high as 5 × 1011 molecule cm−3 (∼20 parts per billion) in the nucleation chamber.


The authors declare no conflict of interest.

1To whom correspondence should be addressed. E-mail: zhang@ariel.met.tamu.edu.
We used the nucleation theorem to estimate the molecular composition in the critical nucleus on the basis of measurements of the vapor phase concentrations and nucleation rates (25). The analyses yielded one CPA and three to five sulfuric acid molecules in the critical nucleus. Quantum chemical calculations have demonstrated the existence of a stable complex between organic acid and H$_2$SO$_4$ molecules, characterized by strong double-hydrogen bonding (23). The stability of the CPA-H$_2$SO$_4$ complex is much higher than those of the H$_2$O-H$_2$SO$_4$, H$_2$SO$_4$-NH$_3$, and H$_2$SO$_4$-H$_2$SO$_4$ complexes; the bonding energy of the CPA-H$_2$SO$_4$ complex is $\approx 4$–7 kcal mol$^{-1}$ higher than those of the H$_2$O-H$_2$SO$_4$, H$_2$SO$_4$-NH$_3$, and H$_2$SO$_4$-H$_2$SO$_4$ complexes. Also, the dipole moment of the CPA-H$_2$SO$_4$ complex (4.6 Debye) is larger than those of the H$_2$O-H$_2$SO$_4$ and H$_2$SO$_4$-H$_2$SO$_4$ complexes, enhancing dipole-dipole interaction with polar molecules such as H$_2$SO$_4$ and H$_2$O (26). The large size, bonding energy, and dipole moment of the CPA-H$_2$SO$_4$ complex likely enhance successive condensations of H$_2$SO$_4$ and H$_2$O molecules to form the critical nucleus.

Fig. 2 shows molecular dynamic simulation of a critical nucleus of the CPA-H$_2$SO$_4$-H$_2$O system. From the CPA-H$_2$SO$_4$ complex to the critical nucleus, the size of the cluster increases from 1.1 to 1.4 nm. It is evident that the sulfuric acid part of the complex is hydrophilic, corresponding exclusively to the growth of the cluster. Conversely, the CPA portion of the complex is hydrophobic that prevents interaction with additional molecules. Except for the carboxylic function group -C(O)OH, the remaining structure of the organic acid is fully saturated. For example, a CPA-CPA dimer also exists that corresponds to a stable complex by forming double-hydrogen bonding between the two carboxylic functional groups from each CPA molecule (23), but such a complex is completely saturated and hydrophobic, inhibiting further cluster growth. The dominant hydrophobic nature of organic acids likely explains the existence of only one CPA molecule in the critical nucleus. This behavior also implies that dimers or heterodimers of organic acids alone are unfavorable for new particle formation because of their hydrophobicity, consistent with our experimental observation of no new particle formation in the coexistence of two supersaturated organic acid vapors.

We performed experiments to analyze the chemical compositions of nano-size particles to gain insight into the nucleation process by using a thermal desorption–ion drift chemical ion-
acid (H$_2$SO$_4$ and H$_2$SO$_4$-H$_2$SO$_4$ dimer) is far more abundant exclusively by condensations of H$_2$SO$_4$ and H$_2$O. While enhancing hyphobicity and lack of stabilization. Thus, the initial growth from CPA on nano-sized particles is limited because of its hydrophilicity and lack of stabilization. In contrast, condensation of low-volatility species on nano-sized particles is greatly suppressed because of enormously elevated equilibrium vapor pressures from the curvature (Kelvin) effect (31). However, H$_2$SO$_4$ molecules condensed on newly nucleated particles are efficiently stabilized by simultaneous condensation of H$_2$O molecules, which prevents evaporation of H$_2$SO$_4$ and leads to an irreversible growth process. In contrast, condensation of CPA on nano-sized particles is limited because of its hydrophobicity and lack of stabilization. Thus, the initial growth from the critical nucleus to the detectable size of 2–3 nm particles occurs exclusively by condensations of H$_2$SO$_4$ and H$_2$O. While enhancing the formation of the critical nucleus by forming a stable complex with sulfuric acid, organic acids contribute negligibly to growth of newly nucleated nanoparticles.

Growth of particles in the size range of 3–30 nm was further studied in the presence of ammonia using a nano-tandem (T)DMA. The sizes of monodisperse particles before and after exposure to ammonia were measured, and the ratio of the two particle sizes yielded the particle growth factor (Fig. 4). Growth of particles of 3–30 nm by exposure to ammonia is negligible over a range of relative humidity conditions. Although it is plausible that the heterogeneous reaction between ammonia and sulfuric acid occurs to produce ammonium sulfate [(NH$_4$)$_2$SO$_4$] on larger particles, ammonium sulfate has a larger density than that of sulfuric acid (30), and its formation does not necessarily contribute to a net increase in the particle size.

In our previous work we have suggested that several aromatic acids, produced from photochemical oxidation of aromatic hydrocarbons, enhance aerosol nucleation (19). The present study extends that work and provides insights into the molecular processes leading to nucleation and growth of nano-sized aerosols over forests. Oxidation of biogenic monoterpenes yields organic acids such as CPA that contribute to new particle formation. The hydrophobic organic acid part in the CPA-sulfuric acid complex results in large stability and enhances growth on the hydrophilic sulfuric acid counterpart to form the critical nucleus. In contrast to the previous studies (24), our results demonstrate that dimers or heterodimers of organic acids alone cannot lead to new particle formation, because since growth from such complexes is prohibited because of their hydrophobicity and the Kelvin effect. By differentiating the processes between nucleation and growth of newly nucleated nano-sized particles, we show that the initial growth from the critical nucleus to the detectable size of 2–3 nm takes place mainly from condensation of H$_2$SO$_4$, along with simultaneous condensation of H$_2$O, but unlikely from condensation of low volatility organic acids or interaction with ammonia. The present analysis of the chemical compositions of newly nucleated aerosols and molecular dynamic simulations provide insights into the molecular information of the critical nucleus, indicating that the critical nucleus likely consists of one CPA and three to five sulfuric acid molecules, along with H$_2$O molecules.
pogenic pollution strongly impacts aerosol formation over pristine
forested areas. Also, organic aerosols are generally considered to be
less hygroscopic, whereas the aerosol hygroscopicity determines
effects on their behavior. Solar radiation transfer and cloud
formation (4). The present laboratory experiments reveal the
dominant role of sulfuric acid in the initial growth of nano-sized
particles, which can influence the hygroscopic characteristics
of biogenic aerosols. The strong interaction between terrestrial biog-
enic and anthropogenic sulfur emissions implies that terrestrial
biogenic aerosols over forested areas likely exert larger direct and
indirect climate forcing than previously recognized.

**Methods**

The laboratory setup for the nucleation experiments consisted of a nucleation
chamber where gaseous aerosol precursors were introduced, an ID-CIMS for
monitoring the concentrations of gaseous species, a nano-DMA for measure-
ments of the size and distribution of aerosols, and TD-ID-CIMS for analysis of
the chemical compositions of aerosols. A detailed description of the nuclea-
sonation system is provided elsewhere (19).

The chemical composition of nano-sized particles was analyzed by TD-ID-
CIMS. Newly nucleated particles generated in the nucleation chamber were
charged and electostatically deposited on a charged platinum wire. The
collected particle mass was subsequently heated/evaporated and analyzed by
using TD-ID-CIMS.

The growth of particles was measured by using nano-TDMA. Aerosols
were produced from the binary H2SO4/H2O nucleation and size-selected
using a nano-DMA (Dp*). Subsequently, the monodisperse particles were
introduced into a growth chamber, where they were exposed to ammonia
time scale of ~30 s. A second nano-DMA was then used to
sample the aerosol flow at the end of the growth chamber (Dp*), and the
ratio of the particle sizes measured by the two nano-DMA yields the growth
factor.

We performed molecular dynamic simulations using the Cerius2 Open Force
Field module (OFF) with the CFF1.02 force field (Accelrys). The molecular clusters
were constructed by using the Cerius2 atomospheric and a unit cubic cell
with 100 nm in dimension using the cluster builder. The cluster with fixed
composition was located at the center of the cube with periodic boundary for
energy minimization to ensure the stability and minimum potential energy of
the model cluster. The minimization was performed using Newton–Raphson algo-
rithms, available in the OFF simulation engine. The minimization process
was found to be efficient and was typically converged in a single minimization run
within a reasonable computational time (within 30 min). It should be pointed out
that, because CFF force field fully accounts for hydrogen bonds in the function
expression, explicit specification was not required for the clusters with ample
hydrogen bonds in this study. The dynamic simulation was performed using the
Verlet leapfrog integrator under fixed composition, isobaric and isothermal
number concentration, pressure and temperature, (NPT) thermodynamic en-
ssemble with periodic boundary condition. The external pressure of the system
was set to zero. The size and the shape of the unit cell were allowed to vary to
accommodate the adjustment of the pressure (kept at 1 atm), and the temper-

ature was controlled by the T-Damping method. An integration time step of 1 fs
was used to ensure the stability and accuracy in the integration process, and the
number of 3 × 10^5 steps was carried out so that a total simulation time of ~30 ns
was obtained, long enough to capture significant representative conformation.

**ACKNOWLEDGMENTS.** We thank the use of the Laboratory for Molecular
Simulations at Texas A&M University, and Dr. Lisa M. Perez for assistance with the
calculations. This work was supported by the Robert A. Welch Foundation Grant
A-1417 and the China National Natural Science Foundation Grant 40728006 and
the Department of Energy Atmospheric Sciences Program (to R.L.M.).

3. Finlayson-Pitts BJ, Pitts JN, Jr (2000) Chemistry of the Upper and Lower Atmosphere:
Theory, Experiments, and Applications (Academic, San Diego, CA).
5. Novakov T, Penner JE (1993) Large contribution of organic aerosols to cloud-
the U.S. on tropospheric chemistry. Proc Natl Acad Sci USA 100:1505–1509.
1:140–149.
2004GL022200.
acidic media: Implications for secondary organic aerosol formation. Environ Sci Tech-
no 40:7682–7687.