Laboratory studies of ice nucleation by aerosol particles in upper tropospheric conditions
Paul J. DeMott, David C. Rogers, Sonia M. Kreidenweis, and Yalei Chen

Citation: AIP Conference Proceedings 534, 451 (2000); doi: 10.1063/1.1361904
View online: http://dx.doi.org/10.1063/1.1361904
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/534?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
The radiative effect of ion-induced inorganic nucleation in the free troposphere

The formation of ice clouds from supercooled aqueous aerosols

Modeling of homogeneous nucleation in the free troposphere and comparison with GLOBE-2 data

Laboratory studies on the potential of tropospheric insoluble aerosol components for heterogeneous ice nucleation

Laboratory studies of ice nucleation in sulfate particles: Implications for cirrus clouds
Laboratory Studies of Ice Nucleation by Aerosol Particles in Upper Tropospheric Conditions

Paul J. DeMott, David C. Rogers, Sonia M. Kreidenweis and Yalei Chen

Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80526

Abstract. Ice formation in sulfate, sulfuric acid and black carbon/sulfate aerosol particles under upper tropospheric conditions was studied using a continuous flow thermal diffusion chamber. No clear difference in the homogeneous freezing conditions (temperature, relative humidity) as a function of degree of liquid sulfate neutralization was found, consistent with most other studies. Results support that homogeneous freezing nucleation cannot alone explain observed conditions for cirrus cloud formation. Some types of black carbon (soot) associated with sulfates in mixed particles will induce freezing in preference to the homogeneous process, but only at quite large particle sizes. Small soot produced from burning a particular jet fuel did not show heterogeneous ice nucleation activity until water saturation conditions were exceeded at upper tropospheric temperatures.

INTRODUCTION

In cirrus clouds, purely soluble particles may freeze as haze particles by a process that is much like the homogeneous freezing of pure water, but modified by solution effects. The temperature and relative humidity (RH) at which this process ensues is expected to depend on the size of particles, their thermo-chemical properties, and their kinetic adjustment to cirrus conditions. Insoluble particles or mixed soluble/insoluble particles may nucleate ice heterogeneously under less stringent thermodynamic conditions. These nucleation processes have been studied for particles of relevant sizes and compositions at cirrus temperatures using a continuous flow ice-thermal diffusion chamber.

EXPERIMENTAL

Aerosol generation systems were designed for sulfate, sulfuric acid, soot and combustion aerosols. Aerosols were characterized for size, concentration, and soluble species composition. A water vapor saturator and sample air precooler were used to assure that particles were liquid-phase prior to entering a continuous flow diffusion (CFD) chamber, where particles adjusted to the low temperature water vapor pressure and the conditions of ice formation were determined. The CFD chamber is described in [2] and [3]. Aerosols were isolated by particle-free flows between ice surfaces held at different temperatures. Particles were exposed to set humidities above ice saturation at temperatures down to -60°C. Sample residence times were > 12 s at room pressure.
Haze and ice particle growth calculations showed these times to be sufficient to nearly achieve Köhler equilibrium between the submicron aerosols and the ambient water vapor concentration and to grow nucleated ice crystals to sizes above a few μm in most cases. The size distribution of particles above 0.3 μm diameter was measured with an optical counter. Fractional freezing conditions were measured as a function of RH. Liquid particle composition was inferred using available water activity data and Köhler theory.

**RESULTS**

Data on the homogeneous freezing of (NH₄)₂SO₄/H₂O and H₂SO₄/H₂O aerosol particles are presented and compared to other recent studies in Figure 1. The data from the current study [2] and from other recent studies [4-8] were used to determine homogeneous freezing point depressions (ΔTₘ), given by,

\[ ΔTₘ = T_{hf(\text{water})} - T_{hf(\text{solute})} = λΔT_m, \]  

where \( T_{hf(\text{water})} \) is the freezing temperature of pure water drops of the same size and at the same nucleation rate as observed at \( T_{hf(\text{solute})} \), \( ΔT_m \) is the equilibrium melting point depression, and \( λ \) is a constant. Depressions are positively valued in this equation. This presentation permits comparison of data sets using different methods and particle sizes and is useful for applying results to numerical cloud models. Other studies on particles with fixed composition include observations of freezing of supermicron drops on a chilled surface [7] and in emulsions [4], and FTIR studies of submicron drops in chilled flow tubes [5,6,8]. The greatest discrepancy occurs within the latter method of study. Otherwise, a value of \( λ \) equal to 2 could be selected for either ammonium sulfate or sulfuric acid with limited uncertainty. This result indicates much deeper supercooling of these solution drops from equilibrium than for pure water drops. Consequently, cirrus formation conditions are not well explained by homogeneous freezing of pure solution drops ([2,4, 6-8]). Results on the effect of sulfate phase state and particle size are described in [2].

Some discrepancies of freezing conditions at unit compositions in Figure 1 appear to be true reflections of nucleation rate differences in the studies and true variation in the constant \( λ \) with nucleation rate. A first analysis of estimated homogeneous freezing nucleation rates is given in Figure 2. The different studies indicate a consistent lowering of the slope of nucleation rate versus temperature for solutions compared to pure water. Reasons for this behavior are under study. The data in this form should be valuable for constraining classical theory and providing more fundamental understanding.

Figure 3 summarizes studies of ice formation on various black carbon (BC) aerosol particles at upper tropospheric temperatures. Some of these results were summarized in [1]. Figure 3 includes additional data on ice formation by soot particles produced from burning jet fuel (Jet Fuel A with PRIST). The data, in most cases, indicate freezing at ice supersaturation conditions that align with those required to homogeneously freeze ice in the liquid portion of the soot aerosols. Only the larger BC
particles with larger acid coatings indicated distinct heterogeneous nucleation activity lower than -53°C. The poor heterogeneous nucleation activity of simulated jet exhaust aerosols is consistent with field observations of contrail formation conditions [10]. Studies are continuing to identify more effective ice nuclei in the upper troposphere and to determine the role of organic carbon particles.

Figure 1. Summary of homogeneous "freezing point" depression versus melting point depression inferred from recent investigations [2-8] of low temperature freezing of sulfates and sulfuric acid aerosols. Data sources are indicated in the legends for a) (NH$_4$)$_2$SO$_4$·H$_2$O, and b) H$_2$SO$_4$·H$_2$O particles. These freezing conditions are relevant for equilibrium droplet conditions, but the slope of the results is useful for making computations of the freezing rates of haze droplets as a function of temperature and instantaneous composition (see text). Adapted from [2].

Figure 2. Ice formation rates (particle$^{-1}$ s$^{-1}$) as a function of temperature and H$_2$SO$_4$/H$_2$O composition estimated from selected data taken in drop freezing (medium and large filled data points: [6]), flow tube (open data points: [8]), and continuous flow diffusion chamber (small filled data points - this study: [2]) studies. Triangles (large), squares, triangles (medium or small), circles and diamonds are data for 0, 13, 16, 18, and 20 ($\pm$1) weight percent (wt%) particles, respectively. Solid lines show the expected freezing rates of pure water droplets based on previous studies, while dashed lines are suggested trend lines of constant wt%. Typical drop sizes were <0.1 $\mu$m in [2], 0.3 $\mu$m in [8] and 7 $\mu$m in [6].
Figure 3. Comparison of the ice relative humidity observed to be required for the formation of ice in 1% of BC based aerosols during the CFD chamber residence time (~12 s here). The thin solid line is the calculated condition for homogeneously freezing the H$_2$SO$_4$-H$_2$O solution on multilayer coated commercial BC particles (mean particle size noted). The dashed and dashed-dotted lines give the calculated homogeneous freezing conditions for monolayer coated BC and combusted jet fuel aerosol particles, respectively. Water saturated conditions are shown by the thick solid line. The data point at -35°C represents the maximum fraction of jet fuel aerosols that would freeze -30°C. Partially adapted from [1].

ACKNOWLEDGMENTS

This work was supported by NSF-ATM9632917, and the NASA Atmospheric Effects of Aviation Program (Jet Propulsion Laboratory Contract 961353). Any findings and conclusions are those of the authors. Y.C. was supported by NASA Earth System Science Fellowship (NGT5-30001). We thank A. Middlebrook, S.L. Clegg, T. Koop, S. Martin, T. Prenni, A. Bertram and D. Cziczo for helpful discussions and/or assistance with experimental design issues.

REFERENCES