**Atmospheric
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Ice nucleation in sulfuric acid/organic aerosols: implications for cirrus cloud formation

M. R. Beaver[1]**, M. J. Elrod**[2]**, R. M. Garland**[1]**, and M. A. Tolbert**[1]

[1]Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, Colorado, 80309, USA
[2]Department of Chemistry and Biochemistry, Oberlin College, Oberlin, Ohio, 44074, USA

Abstract. Using an aerosol flow tube apparatus, we have studied the effects of aliphatic aldehydes (C_3 to C_{10}) and ketones (C_3 and C_9) on ice nucleation in sulfuric acid aerosols. Mixed aerosols were prepared by combining an organic vapor flow with a flow of sulfuric acid aerosols over a small mixing time ($\sim$60 s) at room temperature. No acid-catalyzed reactions were observed under these conditions, and physical uptake was responsible for the organic content of the sulfuric acid aerosols. In these experiments, aerosol organic content, determined by a Mie scattering analysis, was found to vary with the partial pressure of organic, the flow tube temperature, and the identity of the organic compound. The physical properties of the organic compounds (primarily the solubility and melting point) were found to play a dominant role in determining the inferred mode of nucleation (homogenous or heterogeneous) and the specific freezing temperatures observed. Overall, very soluble, low-melting organics, such as acetone and propanal, caused a decrease in aerosol ice nucleation temperatures when compared with aqueous sulfuric acid aerosol. In contrast, sulfuric acid particles exposed to organic compounds of eight carbons and greater, of much lower solubility and higher melting temperatures, nucleate ice at temperatures above aqueous sulfuric acid aerosols. Organic compounds of intermediate carbon chain length, C_4-C_7, (of intermediate solubility and melting temperatures) nucleated ice at the same temperature as aqueous sulfuric acid aerosols. Interpretations and implications of these results for cirrus cloud formation are discussed.

1 Introduction

Cirrus clouds, composed of water ice, form in the upper troposphere and are generally thought to have an overall warming effect at the Earth's surface. Since the occurrence of cirrus has increased beyond that attributable to aviation effects over the last few decades (Fahey and Schumann, 1999), changes in other anthropogenically produced aerosols could be another factor responsible for this increase. A more complete understanding of the critical factors involved in ice nucleation is needed to better model cirrus formation in the upper troposphere and its impact on climate. Sulfate aerosols, ubiquitous throughout the upper troposphere, are known to be important in the formation of cirrus clouds. Several laboratory studies, using a variety of techniques, have established homogeneous ice nucleation conditions for aqueous sulfuric acid and ammonium sulfate aerosols over the tropospherically relevant concentration range (0–50 wt%) (Bertram et al., 1996; Bertram et al., 2000; Hung et al., 2002; Koop et al., 1998; Chen et al., 2000; Cziczo and Abbatt, 2001; Prenni et al., 2001b). There is much less data available for ice nucleation from other inorganic and organic species. However, based on physical data of melting and freezing temperatures of inorganic and organic compounds, Koop et al. (2000) have proposed a model which posits that aerosol water activity is the controlling factor in determining ice nucleation temperatures in the atmosphere.

It is currently known that organic compounds can constitute a significant mass fraction of individual upper tropospheric aerosols (Murphy et al., 1998). It has also recently been observed that atmospheric particles with high organic content are not as efficient at ice nucleation (De-Mott et al., 2003; Cziczo et al., 2004). The effects that organic compounds have on the ability of particles to nucleate ice has only recently begun to be studied in the laboratory. Prenni et al. (2001a) found pure dicarboxylic acids were not

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Correspondence to: M. A. Tolbert
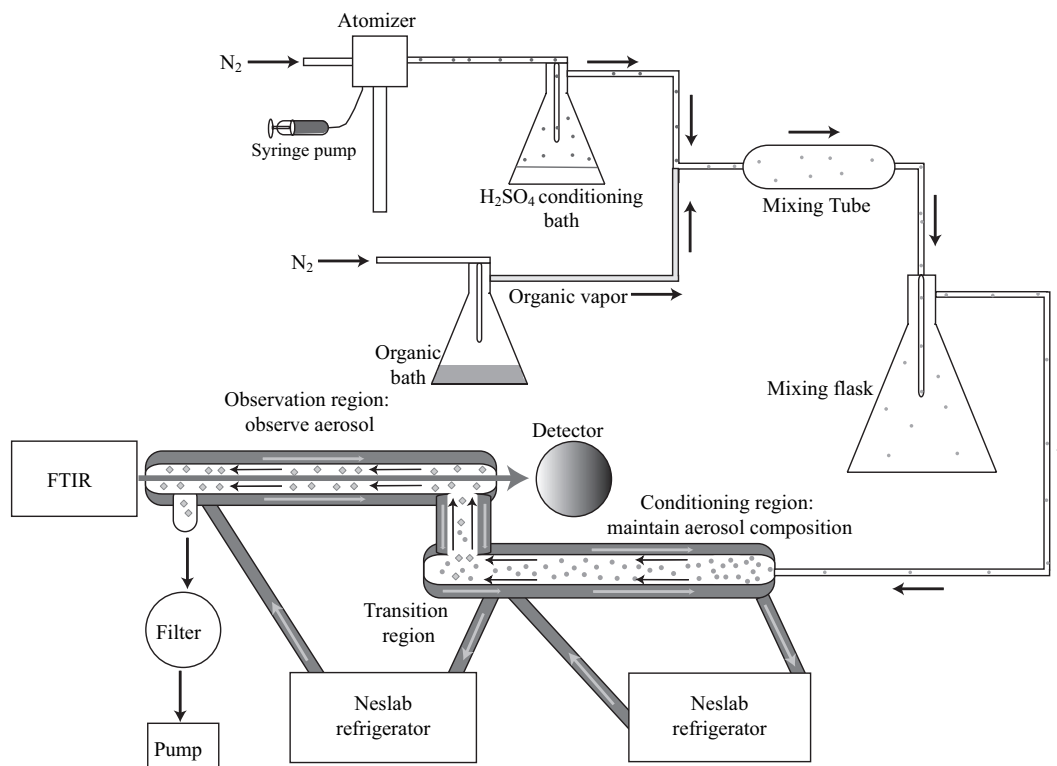(margaret.tolbert@colorado.edu)

Fig. 1. Experimental setup for aerosol generation and measuring ice nucleation in mixed organic/sulfuric acid particles.

as efficient ice nuclei as sulfate particles of the same size. Wise et al. (2004) found that, in general, for internally mixed ammonium sulfate/dicarboxylic acid particles, the water activity of the aerosol could be used to predict ice nucleation conditions, in agreement with the Koop et al. (2000) model. A recent modeling study has investigated the role of dicarboxylic acids in atmospheric ice formation and found that changes in water uptake can affect the size of particles containing organics and thus can explain the observations that organic containing particles are less efficient at ice nucleation (Kärcher and Koop, 2005).

While ice nucleation has mainly been studied for mixtures of dicarboxylic acids with ammonium sulfate, other carbonyl-containing compounds, such as aldehydes and ketones, have been investigated at warmer temperatures to probe acid-catalyzed reactions with sulfuric acid (Iraci and Tolbert, 1997; Jang et al., 2002; Nozière and Riemer, 2003; Michelsen et al., 2004; Garland et al., 2006; Liggio et al., 2005; Nozière and Esteve, 2005; Zhao et al., 2005). An important characteristic of these acid-catalyzed reactions is the ability to form products of lower vapor pressure and solubility as well as higher melting points than the initial reactant compounds. The atmospheric presence of these carbonyl compounds is due to both primary emission from biogenic and anthropogenic sources, and from photo-oxidation of other volatile organic compounds (VOCs). The series of aliphatic aldehydes, from C_3-C_{10}, have been measured

in ambient Los Angeles air samples at levels ranging from 0.41 to 1.09 ppb, with nonanal (C_9) being the most abundant (Grosjean et al., 1996). Ketones such as acetone and 2-butanone were observed at similar levels in the same study. While laboratory studies have provided evidence for possible reaction of these carbonyl compounds with concentrated sulfuric acid at room temperature, there is no data available for ice nucleation when these compounds interact with dilute sulfuric acid aerosols at low temperature.

If the water equilibrium is maintained in sulfuric acid aerosols with significant organic content in the atmosphere, the Koop et al. (2000) water activity model predicts that the ice nucleation temperatures for these complex particles would be unchanged from the aqueous sulfuric acid aerosol case. The Koop et al. (2000) model is also potentially applicable even if aerosols are not in equilibrium with atmospheric water vapor, as long as the aerosol organic content can be determined and related to aerosol water activity. However, field measurements have indicated that mixed organic/sulfate aerosol might be less efficient at ice nucleation (DeMott et al., 2003; Cziczo et al., 2004). One possible explanation for this observation is that the presence of organic compounds modifies the water uptake properties of the aerosol, and serves to sever the equilibrium between aerosol water content and atmospheric water vapor.

Given these possibilities and observations, a series of the straight-chain aliphatic C_3-C_{10} aldehydes, as well as two

Table 1. Measured infrared absorption cross-sections for organic compounds used in this study. The frequency of measurement is also provided. Cross sections for 2-nonanone and decanal could not be determined due to vapor pressure limitations. Infrared absorption cross-sections calculated from NIST data are also shown where available (Thermodynamics Source Database, 2005).

Organic Compound	Frequency used (cm^{-1})	Cross section ($cm^{-1}torr^{-1}$)	NIST Cross section ($cm^{-1}torr^{-1}$)
acetone	2977	9.78E-04	1.45E-3
propanal	2720	2.13E-03	2.00E-3
butanal	2712	2.05E-03	
pentanal	2712	2.49E-03	
hexanal	2712	2.04E-03	
heptanal	2712	8.11E-04	
octanal	2712	1.58E-03	
nonanal	2712	2.04E-03	

ketones, acetone and 2-nonanone, were added to a single composition sulfuric acid aerosol of tropospheric relevance (15 wt% H_2SO_4) to determine the effects on ice nucleation. The findings of the present work indicate that the physical properties of the organics contained in the aerosol may play a key role in determining atmospheric ice nucleation mechanisms and temperatures.

2 Experimental

2.1 Ice nucleation

The experimental apparatus used for measuring ice nucleation from mixed carbonyl and sulfuric acid particles is shown in Fig. 1. Submicrometer sulfuric acid aerosols were generated using an atomizer (TSI Model 3076) with a Harvard apparatus syringe pump. A 30 wt% sulfuric acid solution, prepared with distilled, deionized water, was fed at 0.3 mL/min through the atomizer with pre-purified (PP)-N_2 as the carrier gas. After atomization, the sulfuric acid aerosols were conditioned by passing through a sulfuric acid conditioning bath, which had the effect of adding water to the particles to achieve the desired 15 wt% composition. A flow of organic vapor was merged with the aerosol flow by passing PP-N_2 through a reservoir of organic liquid.

The partial pressure of the organic vapor was controlled by holding the organic reservoir at fixed temperatures ranging from −78°C to +24∘C. In order to quantify the amount of organic to which the sulfuric acid aerosols were exposed, the actual partial pressures of organics were measured in the flow tubes using the infrared absorbance of the organic in the absence of aerosols. Based on a calculation involving aerosol concentration, aerosol growth, and partial pressure of organic, the partial pressure in the absence of and in the presence of aerosols was estimated to be the same, and was used as such throughout this study. Although some infrared absorption cross-sections were available in the literature, infrared absorption cross-sections were separately determined

for most compounds in the present study and used to calculate partial pressures. An infrared gas cell, with a pathlength of 8.25 cm, was filled with the organic compound of interest to pressures ranging from 0.5 to 10.0 torr, measured with a baratron capacitance manometer. All spectra collected were referenced to the background spectrum of the empty gas cell. The absorbance peak height of the aldehydic carbon-hydrogen stretch around 2712 cm^{-1} was used to determine the cross-sections for aldehydes while the aliphatic carbon-hydrogen stretch at 2977 cm^{-1} was used for acetone. Measured infrared absorption cross-sections are listed in Table 1. The NIST database reference spectra were used to calculate cross-sections of 2.00×10^{-3} cm^{-1} $torr^{-1}$ and 1.45×10^{-3} cm^{-1} $torr^{-1}$ for propanal and acetone, respectively (Thermodynamics Source Database, 2005). Our measured values of 2.13×10^{-3} cm^{-1} $torr^{-1}$ and 9.78×10^{-4} cm^{-1} $torr^{-1}$ for propanal and acetone, respectively, agree reasonably well with the NIST database. Cross-sections could not be determined experimentally for 2-nonanone or decanal due to vapor pressure limitations.

The particles and organic vapor were allowed to mix for approximately one minute before entering the aerosol flow tubes. After the mixing period, the organic/sulfuric acid particles entered the temperature-controlled flow tube apparatus similar to that used by Prenni et al. (2001b) and Wise et al. (2004). The aerosol passes through three tubes, with inner diameters of 4 cm that are cooled with recirculated methanol from Neslab refrigerators. The first in the series of flow tubes (90 cm) was held at a constant temperature of −19.0°C (±1.5°C) for all experiments. This conditioning tube served to set and maintain the sulfate to water ratio of the aerosols and to precool the aerosols. Fourier transform infrared (FTIR) spectroscopy was used to observe the aerosols in the third tube (80 cm). The temperature in this observation region was varied over the range necessary to observe ice nucleation, from −30°C to −75°C. A transition tube (∼75 cm) was used between the first and third regions, each end cooled to the temperature of the closest tube, in

order to ensure time for the aerosol to reach the observation tube temperature before detection with FTIR spectroscopy. Flow tube temperatures were measured with thermocouples placed in the aerosol flow. The thermocouples were periodically calibrated against a reference temperature to ensure accurate temperature measurements. Although standard error for thermocouples is $\pm 1.0°$C, we never observed deviation greater than $\pm 0.6°$C from a reference temperature measurement, even at the coldest temperatures used.

The aerosol composition in the observation region was determined using FTIR spectroscopy. The water to sulfate ratio was determined using FTIR spectral calibrations of the ratio of the OH peak (3650–2409 cm^{-1}) to the sulfate peak (1470–820 cm^{-1}) (Anthony et al., 1995; Bertram et al., 1996). The FTIR spectral calibrations were used to verify the water to sulfate ratio remained constant after the addition of the organic compounds. The organic content of sulfuric acid aerosols was determined using a Mie scattering analysis, as contributions from gas phase organics contribute to the organic absorbance bands. This process will be described in detail in the next experimental section.

In a typical ice nucleation experiment, the initial observation tube temperature is set well above the temperature at which the aerosol should nucleate ice. At this temperature, the aerosol composition is verified as described above. Near the freezing point, the temperature of the observation region is decreased in ∼1.5°C increments. The phase of the aerosol is monitored at each temperature using FTIR spectroscopy. Several distinct spectral changes occur near the freezing point including shifts of the -OH stretch, centered at ∼3300 cm^{-1}, to lower frequencies and the H$_2$O librational band at ∼800 cm^{-1} to higher frequencies. Each collected spectrum is subtracted from the previous, warmer spectrum. A modified version of the Hung et al. (2002) formalism is used to quantify ice nucleation temperatures. Instead of the 690–880 cm^{-1} region used by both Wise et al. (2004) and Hung et al. (2002) for ammonium sulfate, a combination of the variance of both the OH stretch and H$_2$O libration regions from (3700–3200 cm^{-1} and 940–660 cm^{-1}) was used to determine ice nucleation temperatures. The product of the variance of the two spectra in these spectral regions was used in order to give them equal weighting. This product was normalized by the change in temperature and then plotted as a function of the temperature of the observation region. The onset freezing temperature was defined when qualitative changes, due to ice nucleation, were observed in both spectral regions. The peaks of these variances are defined as the ice nucleation temperatures in this study. Therefore, onset nucleation temperatures were on average, 1.5–3.0°C warmer than those reported throughout. Although the organics used in this study do contain some absorption features in these spectral areas, no interference with the variance analysis was observed. Steps of 1.5°C were taken to construct the variance plots because 1.5°C was empirically observed to be the approximate uncertainty in the determination of the

freezing temperature, which may be caused by slightly varying aerosol composition. Sulfuric acid aerosol composition was checked, using the infrared calibrations, at the end of most experiments to ensure that a relatively constant base aerosol composition was present throughout the ice nucleation experiment. Organic compounds used in this study were acetone, propanal, butanal, pentanal, hexanal, heptanal, octanal, nonanal, 2-nonanone, and decanal. All chemicals were purchased from Sigma-Aldrich and were of greater than 95% purity. All experiments were conducted using 15 wt% (± 2 wt%) sulfuric acid composition as the precursor aqueous sulfuric acid aerosol.

2.2 Organic content from Mie scattering analysis

In order to quantify the amount of organic incorporated into the sulfuric acid particles, a Mie scattering analysis was performed to determine aerosol diameter before and after organic addition. A Fortran program adapted from Bohren and Huffman (1983) was used to calculate extinction spectra to fit experimental spectra collected at $T_{obs}\sim-49°$C. This temperature limit was imposed by the ice nucleation temperature for sulfuric acid at this composition, as the scattering analysis is valid for unfrozen aerosol only. All calculations were performed assuming spherical particles with a log-normal size distribution and a geometric standard deviation (GSD) of 2.0. The optical constants for sulfuric acid were taken from the work of Myhre et al. (2003) who parameterized them over the concentration range from 12–81 wt% H$_2$SO$_4$ and temperature range from 300–220 K. Due to the absence of optical constants data for the organic compounds at the temperatures used in this study, optical properties of sulfuric acid were assumed in this analysis. To most accurately fit the measured spectra, only the region where scattering features dominate the extinction was used, therefore values at wavenumbers below 2000 cm^{-1} were excluded. Extinction values in the region from 3000 to 2700 cm^{-1} were also eliminated due to interferences from organic CH stretches, when present. The region above 3500 cm^{-1} was weighted more heavily than the remaining portions of the spectrum because the extinction is totally due to scattering in this region. To determine if a distribution of pure organic particles was present in these experiments, investigative experiments were performed where the organic compounds were flowed through the low temperature flow tubes in the absence of sulfuric acid aerosols, and FTIR spectra were collected. Under these conditions, the IR spectra indicated no nucleation of organic particles, i.e. no Mie scattering was observed in the 5000 to 3500 cm^{-1} region. These spectra were also identical to reference gas phase spectra.

The results from this scattering analysis were used to determine aerosol organic molality (m = moles solute/kg of solution). The difference in aqueous sulfuric acid aerosol mean diameters, before and after organic addition, was converted to an aerosol volume change. The increase in aerosol

diameter was assumed to be due only to the incorporation of organic into the aerosol. This volume increase, along with the molecular weight of the organic compound, was used to calculate moles of organic, in order to calculate organic aerosol molaltiy. Then, the total aerosol volume with an estimate of aerosol density based on sulfuric acid, water, and the organic compound densities, were combined with moles of organic to calculate the aerosol organic molarity (M = moles solute/L of solution).

3 Results and discussion

3.1 Scattering results

In evaluation of the Mie scattering analysis, the choice of the geometric standard deviation (GSD) has a strong effect on the calculated aerosol diameter, the value of the GSD has no effect on the calculated *relative* aerosol diameters for two different aerosol distributions. An investigation of the effects of GSD on percent organic is summarized in Table 2. The GSD input to the Mie scattering analysis was varied over the range of 1.4 to 2.6. Fits to spectra of sulfuric acid aerosol both before and after the exposure to 0.13 torr acetone were obtained with the Mie scattering analysis. It can be seen that while the absolute diameters varied widely over the range of GSD, the percent organic remained essentially unchanged. Therefore, since our analysis depends only on changes in aerosol diameter, the choice of GSD has no effect on the calculated results.

The Mie scattering analysis used above assumes a log-normal distribution. However, if the distributions are not log-normal, the calculated relative aerosol diameters might be in error. An alternative Mie scattering analysis (Zasetsky et al., 2004), one not assuming a log-normal aerosol size distribution, was also used to analyze a portion of the data. From the tests with this method, it was found that the aerosol distributions were indeed log-normal. Therefore, the log-normal distribution is a reasonable assumption in this case, and the simpler scattering analysis model of Bohren and Huffman (1983) was used. Overall, in the spectral regions (i.e. the scattering region) used to determine mean aerosol diameter, there is good agreement between the observed and calculated spectra, and the differences in the two spectra are due to the absorption component of the optical constants. This agreement is retained even upon addition of the organic to sulfuric acid aerosols. The variation in diameter of the sulfuric acid aerosol among experiments, before the addition of organic, determined by examining the Mie scattering fits, is 5.0%. In order to determine the uncertainty in the diameters calculated by the Mie scattering analysis, the RMS errors from calculated spectra over a range of diameters close to the best-fit diameter were compared. Then, a RMS error difference of 50% was chosen as an unacceptable fit. This difference translated into an approximate 5.0 nm uncertainty in diameter. This uncertainty was propagated through the percent
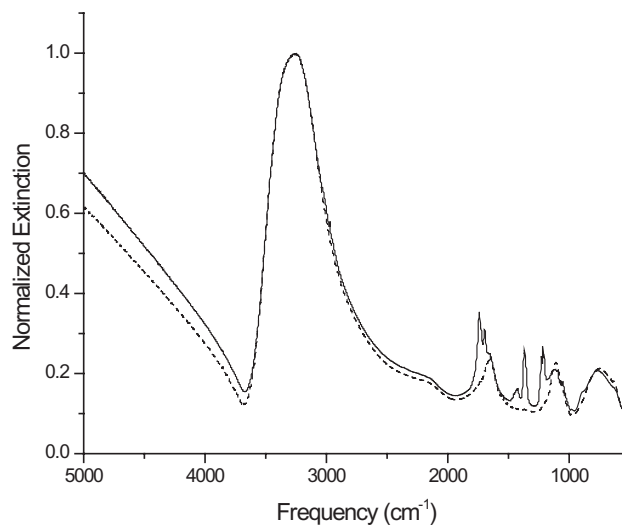

Fig. 2. Infrared extinction spectra for increasing partial pressure exposure to acetone. 15 wt% H_2SO_4 aerosol exposed to 0 Torr (dashed) and 0.435 Torr (solid). The spectra are normalized to maximum extinction. The region above $3500\,\mathrm{cm}^{-1}$ increases in slope with increasing exposure to acetone.

organic and organic molality calculations. However, the accuracy of this method is limited by the assumption that the addition of organic compounds does not significantly modify the optical constants of the aerosol.

Figure 2 shows the increase in the slope of the normalized extinction spectra above $3500\,\mathrm{cm}^{-1}$ upon exposure of sulfuric acid aerosols to increasing partial pressures of acetone. Also, absorption features due to acetone are observed to grow in between 1000 and $2000\,\mathrm{cm}^{-1}$. The increase in slope corresponds to an aerosol size increase caused by increasing the partial pressure exposure of organic vapor. For example, using the procedure discussed above to obtain the organic molality from the diameter difference determined from the scattering observed in the dashed spectrum (no acetone) when compared to the scattering observed in the solid spectrum (0.435 torr acetone) leads to the result that the acetone-exposed aerosol is 5.1 m in acetone, which corresponds to approximately a 30 nm increase in diameter. To determine if the organic uptake was due to acid-catalyzed chemistry, control experiments were performed with aqueous ammonium sulfate (∼30 wt%) as the base aerosol. A qualitatively similar diameter increase was observed, leading to the conclusion that the uptake of the organic is due purely to physical processes (the solubilities of organics in the dilute sulfuric acid and ammonium sulfate aerosols are probably near their pure water values). This result is at odds with the possibility that acid-catalyzed reactions on the time-scale (one minute) and at the temperature conditions (room temperature mixing) of these experiments are responsible for the organic uptake. Also, spectral changes that would be indicative

Table 2. Investigation of the effect of geometric standard deviation (GSD) on calculated diameters (D) and % organic calculated using Mie scattering calculations. Fits to spectra of sulfuric acid aerosol both before and after exposure to 0.13 torr acetone were obtained with the Mie scattering analysis. RMS errors are the difference between the experimental spectrum and the calculated fit.

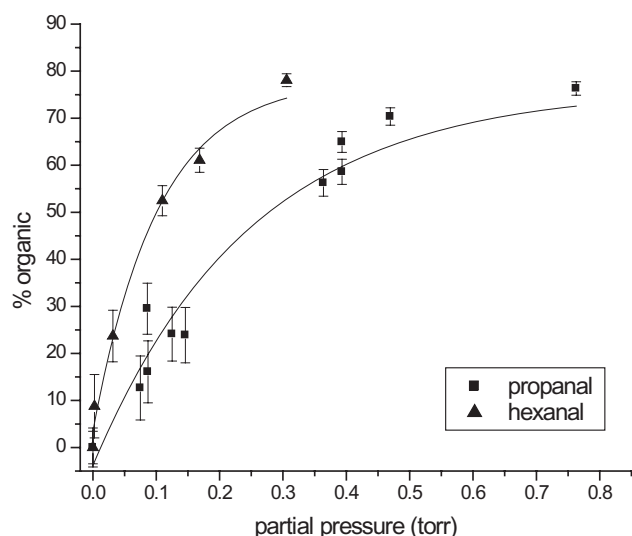| GSD	2.6	2.2	2.0	1.8	1.6	1.4
D (H_2SO_4, nm)	120.8	210.2	278.2	401.8	569.0	794.9
RMS error (final)	0.0192	0.0192	0.0192	0.0192	0.0192	0.0193
D (H_2SO_4 with acetone, nm)	129.0	224.5	297.5	429.3	607.8	848.1
RMS error (final)	0.0151	0.0151	0.0151	0.0151	0.0150	0.0151
% organic	17.9	18.0	18.2	18.0	18.0	17.7

Fig. 3. Dependence of organic uptake (organic content) on organic and partial pressure exposure. Percentage organic determined from Mie scattering analysis, and error bars reflect the uncertainty in this calculation. The curves shown are non-linear fits to the data.

of these acid-catalyzed reactions (i.e. carbonyl stretch shift) were absent. In addition, ongoing bulk kinetics experiments in our laboratory indicate that the one-minute timescale in the present experiments is much too short for acid-catalyzed reactions to occur on 15 wt% sulfuric acid aerosols at room temperature.

The dependence of organic uptake on the identity of the organic compound and partial pressure exposure can be seen in Fig. 3. The lower vapor pressure organic, hexanal, achieves higher uptake at lower partial pressure exposures when compared to an organic of higher vapor pressure, propanal. Percentage organic was determined from Mie scattering analysis, and error bars reflect the uncertainty in this calculation. The curves shown are non-linear fits to the data. It has been assumed that the addition of organic compounds does not significantly modify the optical constants of the aerosol. The error generated by this assumption is not included in the error bars. It can also be seen that the aerosols approach 100%

organic composition at increased organic exposures. Experiments were also performed to observe the organic uptake dependence on observation tube temperature. A consistent size increase was observed to occur with decreasing tube temperature. Therefore, water activity was not fixed in the experiments described in this paper, as it changed with observation temperature, unlike the experiments by Wise et al. (2004) on non-volatile dicarboxylic acids. Also as a result, organic content determinations reported herein must be considered as lower limits as all measurements were made at temperatures above the freezing point of the particles.

3.2 Ice nucleation

The ice nucleation temperature for pure 15 wt% H_2SO_4 aerosol was first measured and compared with previous results. Previous studies have investigated the homogeneous nucleation of 15 wt% sulfuric acid using a variety of techniques including low temperature flow tubes with FTIR spectroscopy (Bertram et al., 1996; Cziczo and Abbatt, 2001; Prenni et al., 2001b), optical microscopy (Koop et al., 1998), and a continuous flow diffusion chamber (Chen et al., 2000). There remains some spread across the ice nucleation results for this composition using these various techniques. The freezing variance plot we obtain for 15 wt% H_2SO_4 is shown in Fig. 4 with a freezing temperature of −54.0°C. Of the previous studies that observed sulfuric acid aerosol ice nucleation temperatures, the result from this set of experiments agrees within error with results from a flow tube study (Prenni et al., 2001b), an optical method (Koop et al., 1998), and a study using the continuous flow diffusion chamber (Chen et al., 2000). These studies report freezing temperatures of −53.0°C for 15 wt% H_2SO_4 aerosol. The Koop et al. (2000) water activity model predicts a freezing temperature of −52.0°C. Therefore, our results, within error (±1.5°C), are in agreement with current literature values for sulfuric acid aerosol, as well as the Koop et al. (2000) model. All subsequent ice nucleation results should be viewed as a change from the 15 wt% sulfuric acid aerosol ice nucleation result of −54.0°C.
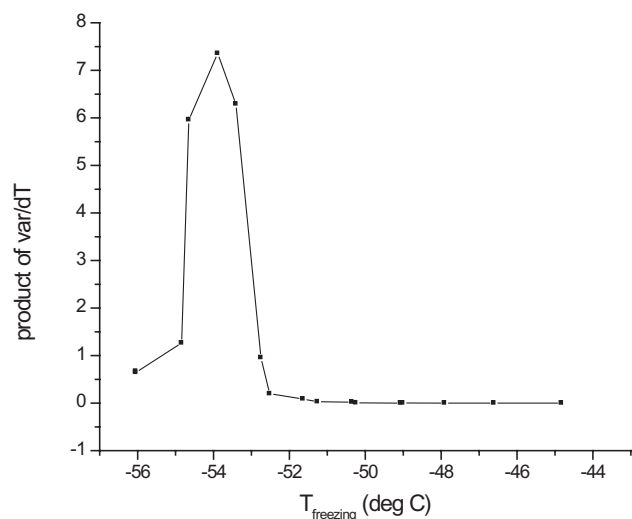
Fig. 4. A variance plot for 15 wt% H_2SO_4 aerosol. $T_{freezing}=-54.0°C$. Error in $T_{freezing}$ was found to be $\pm1.5°C$ due to slight variations in aerosol concentration.

Fig. 5. Freezing temperatures (°C) as a function of propanal partial pressure (Torr). A single-phase aerosol is proposed for exposures <0.15 Torr, a linear fit to this portion of data is shown. At partial pressures above this value, a two-phase aerosol is thought to exist, saturated in propanal.

Fig. 6. Freezing temperatures (°C) as a function of acetone partial pressure (torr). A single-phase aqueous aerosol exists at all partial pressures exposure for which ice nucleation temperature could be determined. A linear fit to the data is shown. Error bars are $\pm1.5°C$.

An extensive ice nucleation study of sulfuric acid aerosols as a function of partial pressure exposure of propanal was conducted, and the results are shown in Fig. 5. In general, there are two regimes into which these results can be divided. At propanal partial pressures less than 0.15 torr, the freezing temperature linearly decreased with increasing propanal pressure, while above 0.15 torr, the freezing temperature remained constant. A linear fit is shown for the data below 0.15 torr. These results can be explained by the existence of a single-phase aerosol at partial pressures below 0.15 torr, where propanal is soluble in the aqueous sulfuric acid aerosol. Therefore, as the partial pressure increases, the molality increases, while the water activity decreases, qualitatively adhering to the Koop et al. (2000) water activity model for homogeneous ice nucleation. The interpretation of the plateauing of the ice nucleation temperatures at about 0.15 torr is that the aerosol apparently reaches the propanal solubility limit. Therefore, any additional propanal added is not soluble and forms an organic phase on the mixed sulfuric acid/propanal aerosol core, and the propanal molality and water activity of the inner aqueous aerosol remains constant. This was tested to partial pressure exposures as high as 1.0 torr. Beyond these exposure levels, quantitative ice nucleation determination became increasingly difficult due to the strong propanal absorption features in the infrared extinction spectra.

From these results, if the 0.15 torr propanal-exposed aerosols are taken as the case where the propanal is dissolved up to its solubility limit, then the results from the Mie scattering analysis indicate that the propanal content of the aerosols, at $-49°C$ is 25%, by volume (4.0 M and 230 g/L). The bulk, room temperature, solubility of propanal in water, as shown
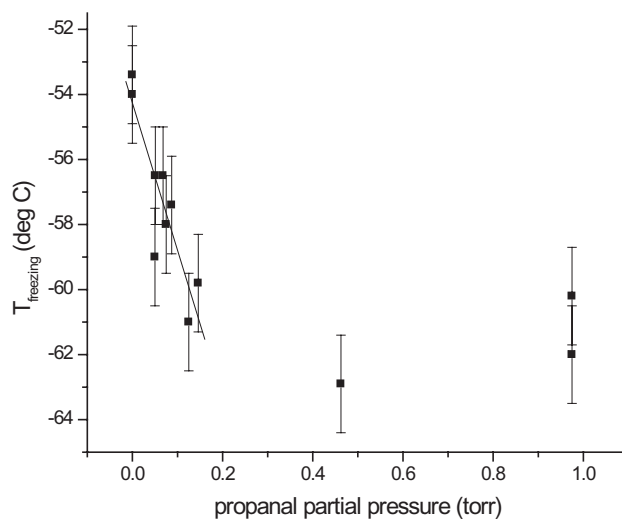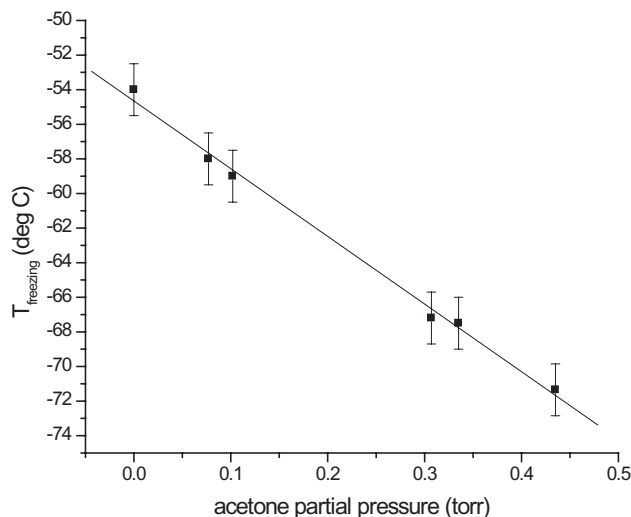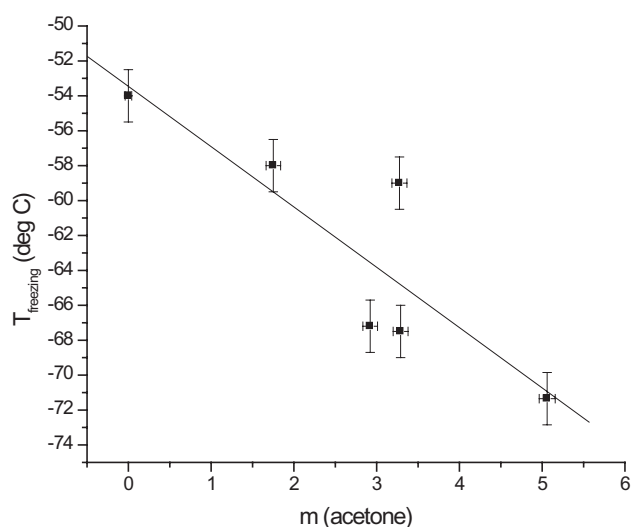
in Table 3 is 306 g/L, which corresponds to 38% by volume (5.3 M). Despite the differences in temperature, this comparison is useful to relate the solubility limit determined by the Mie scattering analysis to that known from bulk measurements.

A similar study of the effect of partial pressure exposure on ice nucleation was also conducted for sulfuric acid aerosols exposed to acetone. Figure 6 shows a plot for acetone similar to that shown in Fig. 5 for propanal, though

Table 3. Physical properties of organic compounds used in this study. Data compiled from Hazardous Substances Data Bank (2005) and Thermodynamics Source Database (2005).

Organic Compound	Melting Temperature (°C)	Water Solubility (mg/L H_2O) @ 25°C
acetone	−95	miscible
propanal	−80	306 000
butanal	−97	71 000
pentanal	−91	11 700
hexanal	−56	6000
heptanal	−43	1550
octanal	−27	560
nonanal	−18	96
2-nonanone	−8	1.4
decanal	−6	20

Fig. 7. Freezing temperatures (°C) as a function of acetone molality. Molality is determined from aerosol size increase as determined by a Mie scattering analysis of infrared extinction spectra. A linear fit to the data is shown. Temperature error bars are ±1.5°C, and molality error bars reflect the uncertainty in the Mie scattering calculation of aerosol diameter.

over a smaller range of partial pressures. In contrast to the propanal case, it can be seen that increasing amounts of acetone cause a decrease in freezing temperatures over the entire range studied. The increased solubility of acetone (as compared to propanal) in sulfuric acid aerosol is the likely cause of the difference. As a result, ice nucleation temperatures could not be measured at any partial pressure exposures higher than 0.45 torr (−71.5°C) due to flow tube cooling system limitations. As more acetone is taken up by the particles, the molality increases while the water activity decreases, again qualitatively adhering to the Koop et al. (2000) water activity theory for homogeneous ice nucleation. In addition, because acetone is more soluble in 15 wt% sulfuric

acid than is propanal, the ice nucleation depression is more pronounced.

Figure 7 shows the same aerosol ice nucleation temperature data as in Fig. 6, but is plotted against aerosol acetone molality. Aerosol acetone molality was determined from the aerosol size increase determined from a Mie scattering analysis of aerosol infrared extinction spectra. In order to quantify the decrease in temperature with aerosol acetone molality, an analysis involving the empirical parameter, λ, was used (Rasmussen and MacKenzie, 1972; Prenni et al., 2001b; DeMott, 2002). The parameter λ is the ratio of the depression of the ice nucleation temperatures of solute-containing droplets to bulk solute-containing solutions each relative to pure water (i.e., λ would be equal to unity in the absence of increased supercooling effects over those of water). According to Eq. (1), the product of lambda, λ, and the melting temperature depression, ΔT_m, equals the freezing temperature depression, ΔT_f (Rasmussen and MacKenzie, 1972; Prenni et al., 2001b; DeMott, 2002). Then, Eq. (2) is the empirical equation for bulk melting point depression due to solute addition (Atkins, 1997).

$$\Delta T_f = \lambda \cdot \Delta T_m \tag{1}$$

$$\Delta T_m = K_f \cdot m \tag{2}$$

This equation relates the bulk melting temperature depression, ΔT_m, to the product of K_f, the solvent freezing point depression constant, and m, molality. In this analysis method, the observed freezing (nucleation) point depression can be related to solute molality, m, according to Eqs. (1) and (2) where K_f is the freezing point depression constant for, in this case, 15 wt% H_2SO_4 and ΔT_f and ΔT_m are the freezing and melting temperature depressions, respectively.

The literature values reported for λ range from 1.4 to 2.2 for various salt solutions, with a typical value of 1.7 (DeMott, 2002). Using 1.7 for λ and K_f for water, 1.86°C/m, the slope of a plot of $T_{freezing}$ versus molality of organic, should be
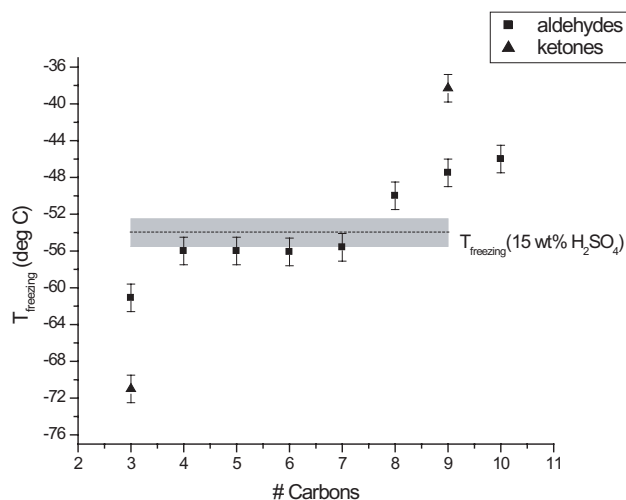
Fig. 8. Freezing temperatures (°C) as a function of organic carbon chain length. Results, except for acetone, are shown for aqueous aerosols saturated with organic. The arrow indicates the possible further decrease in ice nucleation temperature for the saturated acetone/aqueous sulfuric acid aerosol. The water activity of particles with C_4 and longer compounds are likely of constant water activity, though a direct measure of the water activity of the particles was not possible. Error bars on individual data points and the 15 wt% H_2SO_4 freezing result (shaded box) are ±1.5°C.

around −3.2°C/m. The fit to the data from these experiments gives a line with a slope of −3.5°C/m. Alternatively, using the experimental slope and K_f for water, a value of 1.9 is determined for λ, which is well within the typical range. Unfortunately, melting point as a function of solution molality data is not available for these solutions, which is necessary to calculate water activity values. Therefore, a direct comparison to Koop et al. (2000) model predictions is not possible in this case. Despite this, using the empirical relationships described above, the experimental results can be fit.

Because the partial pressure of the organics is measured and the aerosol molarity is determined using the Mie scattering analysis, it is possible to carry out a Henry's law analysis to determine the solubilities of these gases in 15 wt% H_2SO_4. Henry's law is used, in the dilute solution limit, to define the solubility or concentration at equilibrium, of a gas, A, in aqueous solutions, $[A]_{(aq)}$, as related to the partial pressure of the gas above the solution, p_A, according to Eq. (3).

$$[A]_{(aq)} = H_A p_A \tag{3}$$

Henry's law solubilities, H, of 22 000 M/atm and 6600 M/atm were determined for propanal and acetone, respectively, at −50.0°C in 15 wt% sulfuric acid aerosols. No literature Henry's law values exist for propanal in sulfuric acid, while effective Henry's law solubilites for acetone exist in the literature for 40 wt% < H_2SO_4 wt% < 50 wt% solutions at around −50°C (Kane et al., 1999; Klassen et al., 1999; Imamura and Akiyoshi, 2000). These

Table 4. Ice nucleation results versus organic compound added to 15 wt% sulfuric acid aerosols. Ice nucleation was observed for 15 wt% sulfuric acid aerosol at −54.0°C. Partial pressures of organic compounds used were determined using the measured absorption cross-sections. Partial pressure data are not available for 2-nonanone and decanal due to the low vapor pressures of these compounds.

Organic added	Partial Pressure Exposure (torr)	T_f (°C)
acetone	0.35	−71.0
propanal	0.98	−61.1
butanal	0.28	−56.0
pentanal	0.25	−56.0
hexanal	0.34	−56.1
heptanal	0.39	−55.6
octanal	0.15	−50.0
nonanal	0.02	−47.5
2-nonanone	*	−38.3
decanal	*	−46.0

values range from 13 800 M/atm to 21 000 M/atm with errors ranging from 33% to 50%. Also, no reaction is observed in this acetone/dilute sulfuric acid aerosol system, which may also reconcile the lower Henry's law constant for acetone observed here when compared with the Henry's law constant derived from a system in which acetone is reactive (40–50 wt% sulfuric acid) (Kane et al., 1999; Klassen et al., 1999; Imamura and Akiyoshi, 2000). These Henry's law results apply in the dilute solution regime, and cannot, necessarily, be compared with bulk solubility data.

Results from the three carbon organics, propanal and acetone, demonstrate the depression of ice nucleation temperatures due to solubility effects. To further investigate the effects of organics with different physical properties, the effect of increasing carbon chain length was also explored. Results from these experiments are summarized in Fig. 8 and Table 4. All ice nucleation results, with the exception of acetone for which only an upper limit was established, are shown for aqueous sulfuric acid aerosols saturated with the organic (i.e. in the plateau region of Fig. 3). For the organics from butanal (C_4) to heptanal (C_7), ice nucleation temperatures are, within error, essentially the same as for 15 wt% H_2SO_4 aerosols. In contrast, the compounds from octanal (C_8) to decanal (C_{10}) exhibited freezing temperatures higher than that observed for 15 wt% H_2SO_4 aerosols. The water activity of particles with C_4 and longer compounds are likely equal to the value for pure sulfuric acid particles, though a direct measure of the water activity of the particles was not possible.

The physical properties of the organic compounds used in these studies are shown in Fig. 9 and Table 3 and are useful to consider when interpreting these results (Hazardous Substances Data Bank, 2005; Thermodynamics Source
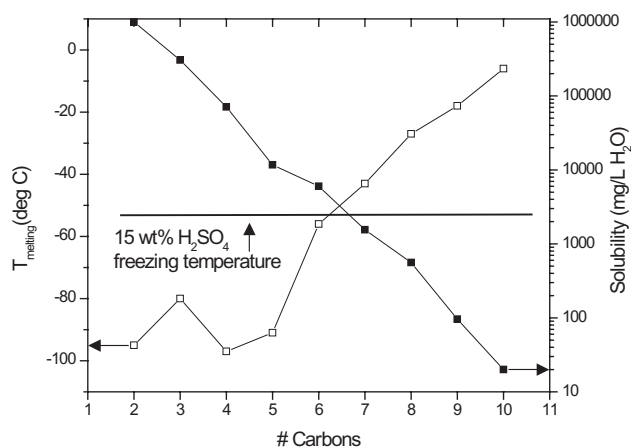
Fig. 9. Melting points (open squares) and solubilities (filled squares) of aldehyde compounds used in this study. Data compiled from Hazardous Substances Data Bank (2005) and Thermodynamics Source Database (2005).

Database, 2005). The difference in the ice nucleation results for acetone and propanal were discussed in the previous section as resulting from the difference in the solubility of the two compounds. In both cases, the high solubility of acetone and propanal likely results in a decrease in water activity. On the other hand, the ice nucleation results for the C_8 to C_{10} compounds can be explained by both differences in the solubilities and melting points of these organic compounds. As can be seen in Fig. 9, these compounds have drastically lower water solubilities and higher melting points than the organic compounds discussed earlier. It is a combination of these physical properties that we believe explain the apparent increase in ice nucleation temperatures over the sulfuric acid base case. Since these longer chain compounds are not very soluble, virtually no decrease in water activity should occur and the aerosol might be expected to nucleate ice at the same temperature as 15 wt% sulfuric acid. However, a coating of these low solubility organic compounds likely forms on the aqueous sulfuric acid aerosols. Unlike the shorter chain compounds, octanal, nonanal, 2-nonanone, and decanal have melting points all above −25°C. As a result, the coating formed on the aerosols freezes at temperatures warmer than the inner aqueous sulfuric acid core (as is dictated by the water activity). Therefore, we believe that ice is heterogeneously nucleated by the frozen organic phase in these cases. The ice nucleation temperatures we find are not the same as the bulk organic melting temperatures, which is likely due to supercooling of the organic phase. Unfortunately, supercooling effects are not well known for these organic compounds, and it is not possible to compare the observed supercooling in our mixed aerosols to supercooling in the pure organic compounds.

The addition of the C_4 to C_7 compounds to aqueous sulfuric acid aerosols causes no change in ice nucleation temper-

ature, relative to the sulfuric acid aerosol base case. Based on solubility properties, these compounds are much less soluble than the C_3 carbonyl compounds, and likely not soluble enough to decrease the water activity of the sulfuric acid core, and, like the C_8 to C_{10} compounds, are likely to form a coating on the surface of the aerosol. However, the freezing temperatures of these intermediate chain length aldehydes are apparently too low, due to the lower melting points and some supercooling effects, to induce a heterogeneous freezing mechanism. As a result, the sulfuric acid core determines the ice nucleation temperature in these aerosols.

Because the time scale for the previously described experiments was much too short to observe acid-catalyzed reactions, an alternative set of experiments was performed in which a bulk solution of sulfuric acid was reacted with butanal for an extended period of time (∼7 days) before being atomized and used for ice nucleation experiments. Acid-catalyzed reaction products were verified using ^{1}H-NMR analysis similar to that described by Garland et al. (2006). Although it was not possible to determine the organic composition of the aerosols in these experiments, the water to sulfate ratio was fortuitously similar to the previous experiments. Therefore, the ice nucleation results could be compared to the ice nucleation temperature of −54°C for the base case of 15 wt% sulfuric acid. Interestingly, these butanal bulk-reacted aerosols nucleated ice at −51°C. This is ∼3°C warmer than the result observed for the gas addition of butanal, C_4, to aqueous sulfuric acid aerosols, while only ∼1°C cooler than that observed for gaseous addition of octanal, C_8, which would be expected to have similar physical properties to 2-ethyl-2-hexenal, the aldol condensation reaction product of butanal. While preliminary, these experiments seem to indicate that acid-catalyzed reactions can indeed result in a change in the mode of ice nucleation for the case of butanal and lead to an increase in ice nucleation temperature.

4 Implications and conclusions

Acid-catalyzed reactions could play an important role in determining which ice nucleation mode might be operative in mixed organic/inorganic aerosols in the atmosphere. In these reactions, shorter chain organic molecules react to create molecules of at least the sum of the carbon chain length. As can be see from Fig. 9, a doubling in carbon chain length from C_4 to C_8, increases melting temperature by 70°C and decreases solubility by a factor of 100. From the interpretation of the present experiments, aqueous sulfuric acid aerosols exposed to butanal nucleated ice by a *homogeneous* mechanism, while octanal-exposed sulfuric acid aerosols nucleate ice via a *heterogeneous* mechanism. Therefore, acid-catalyzed reactions on sulfuric acid aerosols could play a role in transforming organic compounds from those that likely depress or have no effect on ice nucleation temperatures to those that actually elevate the ice nucleation temperatures

through heterogeneous nucleation. However, if no reaction transforms the shorter carbon chain organic compounds to larger organic compounds, the solubility limit will likely not be reached for the shorter carbon chain, highly soluble organic species in the atmosphere (Marcolli et al., 2004).

The present work has shown that addition of organic compounds to 15 wt% sulfuric acid aerosol can lead to a depression, no change, or even an elevation in the ice nucleation temperature. It has been shown that the physical properties of the organic compounds, in particular the solubility and melting point, can be used to interpret the observed ice nucleation temperature. For example, very soluble organic compounds can decrease the water activity of atmospheric aerosols under non-equilibrium conditions (i.e. rapid cooling plumes; Kärcher and Koop, 2005), and lead to a decrease in ice nucleation temperatures. At some concentration, a solubility limit will be reached and a second organic phase will begin to form on the aqueous aerosol. If the freezing temperature of the organic phase is lower than that of the mixed aerosol core, then the organic phase is seen to have no effect on the ice nucleation temperatures. However based on this interpretation, if the freezing temperature of the organic phase is higher than that of the aerosol core, a heterogeneous nucleation mode can occur and higher ice nucleation temperatures will be observed. In general, longer chain organic compounds will induce heterogeneous ice nucleation due to their high melting temperatures. Therefore, knowing the chemical speciation of the organics present in upper tropospheric aerosols is valuable information when predicting their effects on ice nucleation in dilute sulfuric acid aerosols.

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