Phase transformations in sulfuric acid aerosols: Implications for stratospheric ozone depletion

Dan G. Imre, Jun Xu, and Anthony C. Tridico

Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, New York

Abstract. Activation reactions of benign chlorine species (HCl, ClONO2) on aerosols in the winter polar stratosphere set the stage for the spring-time catalytic destruction of ozone leading to the Antarctic ozone hole. Field observations have demonstrated the existence of both solid and liquid particles consisting of H2SO4, HNO3, and H2O. The exact freezing conditions and final composition of the solid aerosols remain the subject of investigations. We present laboratory observations of isolated individual sulfuric acid/water particles under stratospheric temperatures and water vapor pressures. Our experiments demonstrate that this binary system would not freeze unless temperatures were below the water-ice frost point. Upon freezing, we observe H2SO4·8H2O, not the generally invoked H2SO4·4H2O. We suggest that the water-rich octahydrate phase is likely to be one of the high relative humidity forms which is efficient in chlorine activation.

Introduction

Field data [Anderson et al., 1991; Dye et al., 1992; Shindell and de Zafra, 1996; and von Clarmen et al., 1995] provide evidence that heterogeneous chemistry involving stratospheric aerosols transforms the benign chlorine reservoir species (HCl and ClONO2) into highly reactive ozone destroying compounds. These observations indicate a strong correlation between rapid chlorine activation and the presence of polar stratospheric clouds.

Although it has been pointed out that other hydrate forms might also be possible [Zhang et al., 1993], it has generally been assumed that the stable solid phases of the stratospheric aerosols are HNO3·3H2O (Nitric Acid Trihydrate, NAT) and H2SO4·4H2O (Sulfuric Acid Tetrahydrate, SAT), [Abbatt and Molina, 1992a; Abbott and Molina, 1992b; Zhang et al., 1994; Crutzen and Arnold, 1986; Molina et al., 1993; Koop and Karstlaw, 1996], or their ternary mixtures [Fox, 1995]. Present knowledge of heterogeneous chemistry, which is derived from laboratory experiments with bulk materials, indicates that the most effective solid surface for all chlorine activation reactions is ice [Hanson and Ravishankara, 1992; Abbott and Molina, 1992a], while the significantly lower reactivity of SAT and NAT [Hanson and Ravishankara, 1993; Abbott and Molina, 1992b; Zhang et al., 1994; Henson et al., 1996] increases with high relative humidity (RH) and hence phase (vida infra). Rapid chlorine activation was also observed in supercooled bulk liquid sulfuric acid solutions [Hanson and Ravishankara, 1994; Ravishankara and Hanson, 1996; Zhang et al., 1994]. Here as well, the reactivity was found to be a strong function of water content.

Our previous laboratory experiments [Tang et al., 1995] show that phase transformations in aerosols often differ substantially from those in bulk. In this light, the observed sensitivity of the aerosol driven chemistry to particle phase and composition, points to an urgent need for experimental observations on isolated stratospheric aerosols. We present here results of laboratory experiments on phase transformations of single isolated SA/W particles under stratospheric conditions. Our observations suggest that under polar stratospheric temperatures and water vapor pressures, H2SO4·4H2O (SA/W) aerosols will freeze only at temperatures below the water-ice frost point. Upon freezing, we observe a stable octahydrate, H2SO4·8H2O (SAO), not H2SO4·4H2O (SAT), which has been the accepted stable phase. We suggest that the water-rich SAO is likely to be an efficient surface for chlorine activation.

It is important to delineate the differences between the actual stratosphere and our experimental conditions. Most importantly our observations are limited to the binary SA/W system and do not include nitric acid. At temperatures and pressures prevailing in the polar winter stratosphere, nitric acid is expected to be soluble in the SA/W particles changing their properties in the process.

Experimental

The experiments are carried out using a single particle levitation technique, which has been described previously. It is essentially a low temperature version of the one described in [Tang and Munkelwitz, 1984] and a detailed description of the apparatus will be given elsewhere. A single electrostatically charged 5-10μm (diameter) H2SO4·4H2O droplet is suspended in an electrodynamic balance. The H2SO4 droplet is dried under vacuum at ~240K. Once dry, the particle is balanced in a DC field and the voltage required to position the particle at the null-point is noted. The composition under all other conditions is then determined by measuring the change in mass to charge ratio. A single particle can usually be observed for over a week.

A vertically polarized HeNe laser is focused on the particle. The intensity of the scattered light is continuously monitored. The phase (solid or liquid) can be determined from the Mie scattering and phase changes can be readily discerned.

The water pressure in the cell is controlled by the vapor pressure of ice. At the beginning of the experiment, the walls of the chamber are coated with ice and as the temperature is varied, water adsors and desorbs from the chamber walls. The chamber walls are maintained at the same temperature as the particle by using N2 (5 to 10 torr) as a buffer gas. Temperature...
is varied at rates between 0.2 to 2 K/hr. To insure a uniform environment, the temperature is monitored above and below the particle with the difference kept below 0.2K. The error in the temperature measurement of the particle is estimated to be ±1 K.

Experimental Results and Interpretation

The results presented here are a composite of data obtained with four different particles. The data are reproducible from one particle to the next. Figure 1 illustrates our results as they relate to the known bulk equilibrium SA/W phase diagram. In this temperature range, four different solid phases of SA/W have been observed: water-ice, SAO, SAH (H$_2$SO$_4$.6.5H$_2$O), and SAT [Giauque et. al., 1960; Mootz and Merschenz-Quack, 1987]. The tentative bulk stability region for SAO is indicated by a dashed line at 201K. X-ray crystal structure determinations of SAO and SAH are given in [Mootz and Merschenz-Quack, 1987] and a thin film structure attributed to either SAO or a combination of SAT plus ice was observed by infra-red absorption [Zhang et. al., 1993].

The path followed by the particles in our experiment as temperature is changed is indicated by the thick solid line (A-E) in Figure 1. Initially, as temperature is lowered the particle composition and temperature curve is that for a solution maintained at equilibrium with the vapor pressure of ice. Under these conditions, all SA/W particles maintain a metastable homogeneous liquid solution to a temperature as low as 166 (±1) K. Moreover, we repeatedly demonstrated the persistence of the metastable liquid particles under stratospheric temperatures at the water ice frost point by maintaining the particles at a temperature of 190+/−3K for over 3 days: no freezing was observed.

At 166±1K ($f_{P_{exp}}$) a sudden liquid to solid phase transition occurred with, initially, no change in composition. From the mass to charge ratio, we determine the particle composition to be $n = 6.9 ± 0.2$ (where $n = H_2O/H_2SO_4$ is the molar ratio). Since at the freezing point the particle composition does not correspond to any known crystalline phases, to form a single phase of SAH or SAO the particle must lose ~0.4 or alternatively absorb ~1.1 water molecules per H$_2$SO$_4$ molecule. We find that after the liquid-to-solid transition, all particles absorb water ($f_{P_{exp}}-C$) to form a particle of composition identical to SAO ($n = 8.0 ± 0.1$, 40.5 ± 1%SA). This solid-solid transformation requires 4 to 5 hours to complete at 166K. This behavior could not have been predicted on the basis of the bulk phase diagrams. Moreover, it cannot be observed under flow conditions where the particle can be observed for a short time only.

Once formed, SAO appears to be completely stable along the ice-water line, with no changes observed up to 212.7 ± 1K, at which point all particles deliquesce by absorbing water to form the 37%SA solution (D-E). In an effort to test the long term stability of SAO under stratospheric temperatures, we have maintained SAO particles for four days at 190K ± 4 demonstrating that SAO, once formed, does not transform to SAH or SAT under these conditions. The observed deliquescence point is 1.7K higher than the deliquescence point of SAH (211K). We conclude from the deliquescence point and the constant mass of the particle that under the experimental trajectory SAO remains stable from 166K to 212.7K.

The Binary SA/W System Under Stratospheric Temperatures and Water Pressures

We present below a qualitative description of the expected behavior of SA/W particles subjected to cooling and warming under temperatures found in the polar stratosphere. The graphic representation of this discussion is shown in Figure 2.

The freezing line. Our experiments have already demonstrated that as long as the temperature is above 166K, freezing of SA/W can occur only at water pressures higher than the ice frost point. This point established, it would now be advantageous to develop an empirical model, even if approximate, of the freezing behavior of SA/W particles under any arbitrary path in temperature and water pressure.

In a recent paper, the freezing of SA/W aerosols in a flow system were observed at temperatures from 240 to 170K [Bertram et. al., 1996]. The observed freezing conditions in this experiment form a well defined freezing line in the temperature composition domain. This line is in qualitative agreement with the freezing line we derive below, although because the water vapor pressure in their experiments was not determined, a quantitative comparison with our results is difficult. Other experimental studies, on bulk materials in contact with cell walls, have also attempted to determine the freezing conditions

Figure 1 Dependence of composition on temperature of sulfuric acid-water particles at water vapor pressure equal to the vapor pressure of water-ice. The experimental cooling (A-f$_{P_{exp}}$-C) and warming cycle (C-D-E), thick solid lines, is superimposed on the sulfuric acid/water phase diagram (thin lines). The liquid particle (open circles A-f$_{P_{exp}}$) freezes at 166 ± 1K ($f_{P_{exp}}$) and absorbs water ($f_{P_{exp}}$-C) to produce H$_2$SO$_4$.8H$_2$O. This phase remains stable during warming (C-D) until 212.7 ± 1K, where it deliquesces by absorbing water (D-E). The horizontal lines at 211K, and 219K indicate incongruent melting temperatures. The dashed line at 201K is a tentative melting line for H$_2$SO$_4$.8H$_2$O.
Middlebrook et. al., 1993; Zhang et. al., 1993. Several reported [Jensen et. al., 1991; Larsen, 1994; Luo et. al., 1994], however, their accuracy is limited due to the lack of experimental and stratospheric freezing points. fPcxp and fPt are stratospheric conditions with the 2 x 10^-4 torr path labeled A. Theoretically derived SA/W freezing lines have been previously generated according to Mirabel [1996], marks the range of stratospheric conditions with the 2 x 10^-4 torr path labeled A through F (liquid phase - o, solid phase - •). For reference the experimental path (....) from Figure 2 is also reproduced. The solid thick line represents a trajectory for an air parcel above the SA/W freezing temperature is a horizontal line reflecting a nearly constant water vapor pressure. In contrast, over the same range of conditions the particle composition changes greatly with decreasing temperature even prior to freezing. As the temperature decreases, for a fixed Pw, the relative humidity increases rapidly resulting in accretion of water by the particle with concomitant dilution of sulfuric acid from ~60%SA at 200K to ~40%SA at 190K. At 188K, this trajectory intersects our proposed freezing line (fp) which is ~1K lower than the water-ice frost point. Under higher water vapor pressures such as those found in the arctic, the freezing temperature is expected to be ~193.5K (at 100mb). According to the phase diagram, these trajectories cross the freezing line in the SAO plus water-ice region (see Figure 1), therefore, we expect SAO and ice to form.

The phase diagram and recent data [Bertram et. al., 1996] suggests that the first step involves the formation of an ice precipitate in a ~37.5%SA/W solution. The presence of an ice nucleus induces the metastable solution to crystallize [Ohtake, 1993; Koop et. al., 1995] producing a SAO + ice particle. This process would drive the water vapor pressure to the frost point, where we have demonstrated SAO to be the stable phase.

As noted in Figure 2 the freezing point along the stratospheric path (fp) is in a region where the gas phase is supersaturated with respect to ice, (RH < ~1.15). The presence of the newly formed solid particles would provide suitable surfaces necessary for ice condensation, producing an ice coating over SAO nuclei (fp-C). Because the larger particles freeze first, they serve as nucleation sites and lower the water pressure to RH = 1, inhibiting further freezing of the smaller particles. The fraction of particles that freeze depends on the cooling rates and the particle size distribution. This mechanism is supported by field data that shows a mixture of liquid and solid particles within a single air parcel. The frozen particles can grow to a size large enough to precipitate resulting in stratospheric dehydration.

Subsequently, as temperature rises above the water-ice frost point, the condensed water-ice coating would be expected to evaporate (C-D) leaving behind a SAO particle. As we have demonstrated SAO is the stable form at the frost point. Our experiments, however, leave open the question as to what occurs upon further warming. An increase in temperature at constant water vapor pressure produces a dryer stratosphere. As the RH decreases, the water-rich SAO will become unstable. Depending on the temperature where this occurs (marked in Figure 2 by ?) a solid-solid phase transition to SAIl and upon further warming from SAH to SAT might be induced.

Conclusions

Using laboratory observations of isolated sulfuric acid particles, we have developed a picture of the behavior of such particles under stratospheric temperatures and water vapor pressures. We have generated a freezing line, which is based entirely on observations of aerosol behavior. This line indicates that in the range of stratospheric temperatures and water vapor pressures the SA/W particles freeze at a temperature close to the ice frost point but ~1K lower. The solids that form under these conditions are ice and sulfuric acid octahydrate, not the

Figure 2. Stratospheric cooling/warming path in a plot of temperature vs. particle composition. The shaded area, generated according to Mirabel [1996], marks the range of stratospheric conditions with the 2 x 10^-4 torr path labeled A through F (liquid phase - o, solid phase - •). For reference the experimental path (....) from Figure 2 is also reproduced. The experimental and stratospheric freezing points, fPcxp and fPt, are at the intersection of the corresponding paths with the freezing line (——). The dotted line (fp-C) indicates water-ice condensation. The path (C-F) depicts warming, (C-D) evaporation of the water-ice coating, (D-?) sulfuric acid octahydrate region, and (?) indicates an expected H2SO4·6.5H2O transition upon warming.

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Molina et. al., 1993; Beyer et. al., 1994; Song, 1994; Middlebrook et. al., 1993; Zhang et. al., 1993]. Several theoretically derived SA/W freezing lines have been previously reported [Jensen et. al., 1991; Larsen, 1994; Luo et. al., 1994], however, their accuracy is limited due to the lack of thermodynamic data.

We adopt the simplest first order approximation, connecting the field observations of the freezing of SA/W droplets in campaigns designed to study cirrus cloud formation [Heymsfield and Milosovich, 1993; 1995] and our point at 166K. We assume that the freezing line can be approximated by a straight line in a log(Pw) vs. 1/T plot (where Pw is the water vapor pressure in torr).

A representation of the freezing line in the composition-temperature domain (Figure 2) is derived using the vapor pressure, composition, and temperature relationship for SA/W from [Mirabel et. al., 1996].

The cooling and warming pathway. The range of water vapor pressures and temperatures in the stratosphere, where ozone depletion occurs, is represented by the shaded area in Figure 2. The overlap between the experimental path and the shaded area marks the stratospheric conditions that are reproduced in our experiments. The solid thick line represents a trajectory for a water pressure of 2 x 10^4 torr.

From the gas phase perspective, the cooling trajectory for an air parcel above the SA/W freezing temperature is a horizontal line reflecting a nearly constant water vapor pressure. In contrast, over the same range of conditions the particle composition changes greatly with decreasing temperature even prior to freezing. As the temperature decreases, for a fixed Pw, the relative humidity increases rapidly resulting in accretion of water by the particle with concomitant dilution of sulfuric acid from ~60%SA at 200K to ~40%SA at 190K. At 188K, this trajectory intersects our proposed freezing line (fp) which is ~1K lower than the water-ice frost point. Under higher water vapor pressures such as those found in the arctic, the freezing temperature is expected to be ~193.5K (at 100mb). According to the phase diagram, these trajectories cross the freezing line in the SAO plus water-ice region (see Figure 1), therefore, we expect SAO and ice to form.

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tetrahydrate previously accepted. SAO is the stable form under high RH conditions, although SAT may form upon warming as a consequence of SAO to SAH and SAH to SAT transitions.

The observation of a stable water-rich crystalline phase provides insight into the chemistry of the solid phase. Laboratory experiments have shown that bulk water-ice surfaces are extremely effective at chlorine activation whereas SAT, unless under high RH, is rather ineffective. Since we have shown that at RH1 = 1 the stable form is SAO, we propose that the observed reactivity of SAT under high RH is a result of a formation of a higher hydrate surface layer. The explanation for the large differences in reactivity among the hydrates can be found in their crystal structures. According to [Mootz and Merschenz-Quack, 1987], H2SO4:4H2O (SAT) is best considered as the anhydrous acid (H2O)2SO4, whereas SAH and SAO are viewed as hydrated acids (H2O)2(H2O)2SO4:1.5H2O and (H2O)2(H2O)2SO4:4H2O (the tetrahydrate of the anhydrous SAT), respectively. The chlorine activation reaction, ClONO2 + H2O → HNO3 + HCl, clearly requires water as a reactant, thus explaining the high efficiency of ice, and the inefficiency of the anhydrous SAT. Similarly, we would expect SAO to be highly reactive due to its free water content.

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D. G. Imre, A. C. Tridico, and J. Xu, Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11793-5000.

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