LABORATORY SIMULATIONS OF NAT FORMATION APPROACHING STRATOSPHERIC CONDITIONS

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Abstract. Previous laboratory studies have established the stability conditions of nitric acid trihydrate (NAT), of which type I polar stratospheric cloud (PSC I) particles are thought to be composed. However, NAT samples in lab studies were almost always formed under conditions very different from those of the stratosphere. In order to better understand the in situ growth of PSC I particle populations, samples of water and nitric acid were deposited under conditions of temperature and pressure which more closely approximate the polar stratosphere. The compositions of the solids, measured shortly after deposition, depended on the H_2O:HNO_3 ratio in the vapor from which the solids were condensed. Solids formed from vapor mixtures that approached stratospheric contained significantly less HNO_3 than the 25 mol% expected of NAT.

Introduction

The role of type I polar stratospheric clouds (PSC I) in chlorine catalyzed ozone destruction has been widely documented. Laboratory studies (Hanson and Mauersberger, 1988) have provided strong evidence that the PSC I are composed of particles condensed from water and nitric acid in a 3:1 ratio to form nitric acid trihydrate (NAT). The phase diagram of the nitric acid/water system has been used to successfully explain the appearance of PSC I as stratospheric temperatures fall to within 3-7 K of the ice point (Fahey et al, 1989).

On the other hand, some questions about the nature of PSC I particles remain. Several recent in situ studies of stratospheric gases and cloud particles have shown the existence of higher HNO_3 pressures and lower PSC I populations than would be expected on the basis of the laboratory data on NAT vapor pressures. This is especially true in the winter arctic stratosphere (Arnold, et al, 1992; Schlager et al, 1990; Gandrud et al, 1990). In addition, some laboratory studies of condensed water and nitric acid solids show compositions other than what

one would expect of the trihydrate (Hanson and Mauersberger, 1988). Under certain conditions, H_2O and HNO_3 appear to condense into a metastable dihydrate, or NAD (Tolbert and Middlebrook, 1990; Worsnop et al, 1992; Koehler et al, 1991). A previous study (Marti et al, 1991) found that HNO_3 content in a PSC particle could determine its ability to absorb and adsorb HCl, making it important to resolve these uncertainties about composition.

Because PSC particle microphysics is difficult to study in situ, we must rely upon laboratory measurements. However, most laboratory studies of HNO_3 ices have been performed under conditions far different from those of the stratosphere. At 70 mb over the polar regions, the partial pressure of H_2O is about 2 to 3×10^{-4} torr; that of HNO_3 ranges from 3 to 4×10^{-7} torr (Kawa et al, 1992; Schlager et al, 1990; Fahey et al, 1989). The resulting H_2O:HNO_3 ratio is around 850:1 in the lower arctic stratosphere, and about 700:1 in the antarctic stratosphere outside of the springtime chemically perturbed region. Under these conditions, the ice point is between 189 and 191 K, and NAT should condense near 197 K. The partial pressure of HNO_3 is much lower, and the H_2O:HNO_3 ratios much higher, than those used in several laboratory studies (Ritzhaupt and Devlin, 1991; Hanson and Mauersberger, 1988; Marti et al, 1991; Tolbert and Middlebrook, 1990). Samples of nitric acid hydrates have been prepared by direct dosing of surfaces cooled to temperatures below those found in the stratosphere (Koehler et al, 1992; Tolbert and Middlebrook, 1990). Other lab studies have formed NAT by exposing predeposited water ice to HNO_3 vapor (Tolbert and Middlebrook, 1990; Worsnop et al, 1992) or HNO_3/H_2O mixtures (Hanson, manuscript in preparation). Since PSC I typically form a few degrees higher than ice clouds and would thus precede ice formation as air temperatures dropped, NAT formation upon ice is probably not the path taken by most PSCs.

In order to bridge the gap between laboratory and stratosphere, a systematic study was begun to model the

growth of stratospheric cloud particles in the laboratory. This paper reports our first measurements of the initial composition of nitric acid solids, formed under conditions that approached those in the stratosphere. Future work will measure the vapor pressure behavior of solids condensed in a like manner, and attempt to track any evolution of solid composition with time.

Experiment

Samples were condensed from vapor phase mixtures of H_2O and HNO_3 in nominal ratios of 3:1, 10:1, 30:1, 100:1 and 300:1. Water vapor was kept at $3x10^{-4}$ Torr for all ratios to simulate the approximate ambient $p(H_2O)$ at 100mb. Vapor mixtures were produced and analyzed with the apparatus in figure 1. Water and nitric acid vapors were drawn into a five liter sphere from aqueous reservoirs and analyzed for impurities with a mass spectrometer beam system described elsewhere (Mauersberger and Finstad, 1979). Pressure measurements were performed with a calibrated capacitance manometer and temperature measurements with two calibrated platinum resistance thermometers. The vapors were condensed on the inner surface of a glass cell cooled by a temperature controlled bath. Bath temperature was lowered from about 210 to 195 ± 1 K at a rate of about 0.5 to 3.0 K/min. Some samples were deposited at 192.5 K--see below.

At the close of deposition, the sample cell was isolated and the gas analysis sphere cleared of uncondensed vapor. The sample was then evaporated and allowed into the sphere for gas analysis by the mass spectrometer. A calculation of $[HNO_3]/\{[HNO_3]+[H_2O]\}$ yielded the composition, expressed as mole percent (mol%) of HNO_3.

The composition measurements of the mass spectrometer beam system had an accuracy that depended upon the sample size. In order to maintain +/- 5% accuracy, samples had to be no smaller than 0.2 micromoles in size. As a result, samples were deposited long enough to meet or exceed the minimum size, which in turn established a minimum deposition time. The minimum time depended upon the deposition speed, which was much higher for HNO_3 rich mixtures than for those with less HNO_3. Specifically, 3:1 HNO_3/H_2O vapor mixtures required a minimum of five minutes deposition at 195K, while at least sixty minutes were needed for the.100:1 and 300:1 mixtures at 192.5K. The vapor content over the growing solid was continuously monitored for the duration of deposition to maintain the desired partial pressures of H_2O and HNO_3.

The cold glass condensation cell had approximately 4 cm^2 of available surface area. A one watt heater was used during deposition to keep the rest of the cell free of deposited material. Even with this precaution, however, water vapor can still adsorb upon the glass

independent of a growing NAT crystal, affecting composition measurements. To measure this source of error, water vapor was allowed into the cell at a few degrees above the ice point in the absence of HNO_3. The water adsorbed on glass under these conditions amounted to no more than 10% of the mass of the smallest sample.

Results and Discussion

Measurements of the composition of the solids are shown in figure 2. These measurements are of initial composition, obtained from samples allowed to grow to roughly the minimum size as described in the Experiment section above. The data represent a snapshot of the solids shortly after formation from the vapor phase. Some of the samples grown from mixtures of H_2O and HNO_3 in roughly 3:1 ratios exhibited very high initial HNO_3 mole fractions (written hereafter as $[HNO_3]$), approaching 50 mol%, which would be expected of nitric acid monohydrate. Three such samples exhibited compositions close to that expected of the dihydrate, 33 mol%. Samples formed from vapor ratios near 10:1 and 30:1 tended to have $[HNO_3]$ clustered around 33 mol%, suggesting that these solids were deposited as dihydrates. However, several 30:1 samples were intermediate or tended toward a 25 mol% $[HNO_3]$, which would be expected of stable trihydrates. The data seem to confirm what several researchers have suggested on the basis of vapor pressure and FTIR data: solids condensed from water and nitric acid vapor may initially form dihydrates as well as trihydrates, even when the vapor phase $H_2O:HNO_3$ ratio is well in excess of
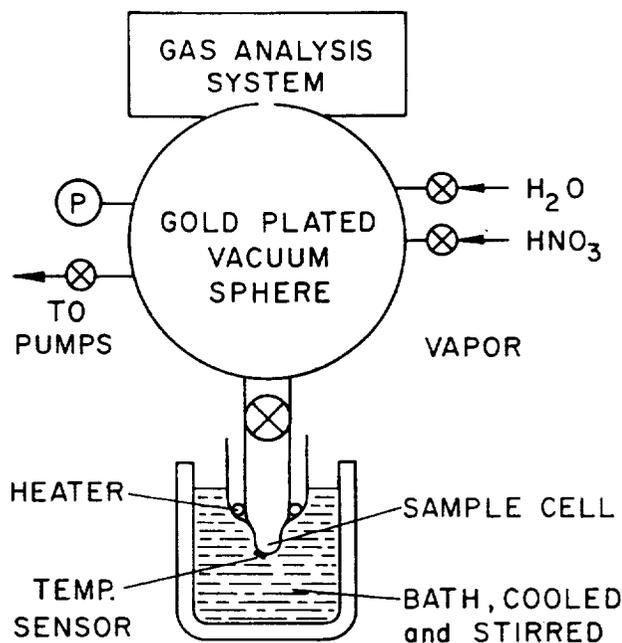

Fig. 1.   Apparatus for composition measurements.

three to one. The dihydrate is thought to be metastable, with relaxation to the trihydrate likely over some unknown time scale.

Two samples grown from 100:1 vapor mixtures clustered around the 25 mol% level, while one sample showed a [HNO$_3$] lower than 20 mol%. Samples repeatedly grown from vapor mixtures with H$_2$O:HNO$_3$ ratios near 300:1 showed surprisingly low [HNO$_3$], far less than would NAT. This low HNO$_3$ content suggests a solid solution or homogeneous crystalline solid with a water/nitric acid ratio of about 5 or 6 to 1, or a mixed crystalline solid consisting of NAT and ice, as has been reported by Ritzhaupt and Devlin (1991).

The data show that as the vapor mixture grows more dilute, the less water rich hydrates (mono- and di-) are less likely to form. The atmosphere, with its very high H$_2$O/HNO$_3$ ratios and low HNO$_3$ pressures, would be very unlikely to favor formation of anything richer in HNO$_3$ than the trihydrate.

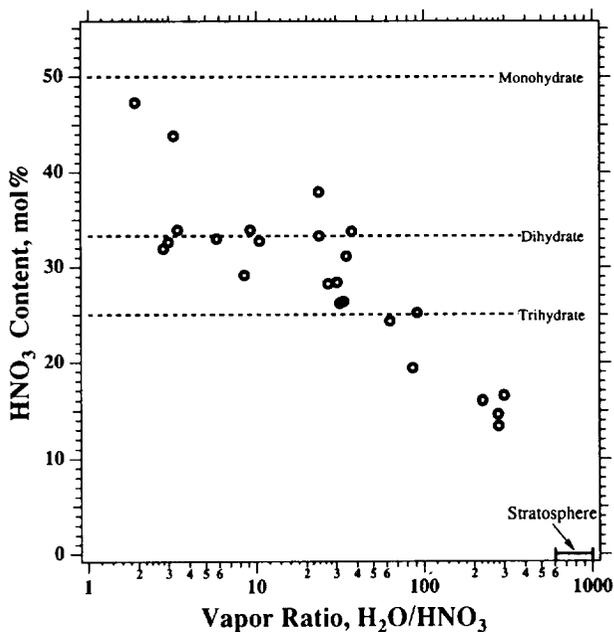Fig. 2.   Initial compositions for solids formed out of H$_2$O/HNO$_3$ vapor mixtures, in ratios ranging from about 2:1 to 300:1. Composition is given as HNO$_3$ content in mol%. The ratios expected for monohydrate, dihydrate, and trihydrate are given as dashed lines. The conditions expected for the stratosphere are given as a range on the x axis.

The possibility exists that the solids as initially formed may not actually be crystalline hydrates. Instead, they may be amorphous solid solutions with the approximate composition of hydrates, as some have suggested (Hamill et al, 1988; Rosen et al, 1989). To distinguish between the two, vapor pressure measurements are necessary, since a true trihydrate should show the well known NAT pressures, while an amorphous solid with the same composition would presumably have higher vapor pressures. Experiments are currently underway to investigate the H$_2$O and HNO$_3$ vapor pressures of solids formed out of a range of water/nitric acid ratio mixtures.

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