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AEROSOL NUCLEATION IN THE WINTER ARCTIC AND ANTARCTIC STRATOSPHERES

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Abstract. We calculate the formation rate of sulfuric acid - water aerosol particles as a function of altitude for the conditions of the winter Arctic and Antarctic stratospheres. The theoretical results indicate that sulfate particle formation can occur in the polar winter stratosphere. Conditions for new particle formation are increasingly favorable as the altitude increases between 20 and 30 km because of the decrease in surface area of pre-existing particles and increasing sulfuric acid vapor supply. The theoretical predictions are consistent with observations of a high altitude CN layer over Antarctica in the spring. Available vapor pressure data indicate that ternary system particles composed of sulfuric acid, nitric acid and water are not thermodynamically stable under winter stratospheric conditions.

Introduction

Polar stratospheric clouds are believed to be composed of a frozen solution of nitric acid and water, perhaps in the trihydrate phase, $HNO_3 \cdot 3H_2O$ (Toon et al., 1986, Crutzen and Arnold, 1986). It is reasonable to assume that this nitric acid aerosol is formed by vapor deposition onto background frozen sulfuric acid aerosol particles.

Background stratospheric aerosol particles are composed of a sulfuric acid solution of about 75% H_2SO_4 and 25% H_2O by weight. A bulk solution of this composition will freeze at about 230 K, small particles will probably be considerably supercooled (Hamill et al., 1988). Measurements of particles collected on wire impactors and other techniques indicate the particles have a mean radius of about 0.1 μm and a number density of about $10/cm^3$. The number density of the nitric acid droplets in the polar stratospheric clouds is also of the order of $10/cm^3$ (Wilson et al., 1989; Ferry et al., 1989) suggesting that PSC particles are formed by vapor deposition of nitric acid and water onto a frozen sulfuric acid core. Poole and McCormick, 1988 and Toon et al. 1990, have modeled this process and have achieved good agreement with observation. The condensation of HNO_3 vapor onto pre-existing sulfuric acid particles is expected to occur at a temperature of about 196 K.

In this paper we do not consider the condensational growth of the PSC particles but rather the formation of new sulfuric acid particles by homogeneous nucleation. Wilson et al., 1989 and Hofmann et al., 1989 report on CN measurements taken in the polar winter stratosphere. Wilson notes the CN mixing ratios suggest new particle production. Hofmann's measurements indicate a high altitude CN layer which increases with altitude. Our calculations of enhanced nucleation rates in the winter stratosphere are consistent with these observations.

Nucleation of Sulfuric Acid Particles

The nucleation of sulfuric acid-water solution aerosols under "normal" stratospheric conditions has been considered by a number of investigators. The nucleation of binary aerosol particles (such as H_2SO_4 - H_2O) under stratospheric conditions was first carried out by Hamill, Kiang, and Cadle (1977). Later other investigators, such as Yue and Deepak (1982) carried out parametric studies of nucleation at different values of temperature and relative humidity. Evaluating nucleation rates for typical mid-latitude conditions, Hamill et al. (1982) found that nucleation rates in the stratosphere are extremely small. A typical value at 17 km is 10^{-20} particles per cm^3/sec. The only region of significant new particle formation is the upper troposphere, suggesting that the sulfate aerosol population of the stratosphere is maintained by the upward diffusion of newly nucleated particles. The calculated nucleation rate at 14 km was of the order of 10^{-8} particles per cm^3/sec. This nucleation rate is somewhat greater than the rate of particle formation required to maintain a steady state stratospheric aerosol population, assuming a number density of $10/cm^3$ and a lifetime of one year. However, the polar winter stratosphere is considerably colder than the mid-latitude stratosphere and one might expect nucleation rates to be enhanced there. We will show that this is indeed the case.

Homogeneous nucleation of sulfuric acid droplets occurs if the Gibbs free energy of the liquid droplet is lower than the Gibbs free energy of the condensing vapor. The Gibbs energy of a liquid droplet has two terms, one is the "bulk" term which is proportional to the volume of

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the particle and which will be negative if the gas phase is supersaturated. The other term is the "surface" term which is the product of the surface tension and the surface area. This term is always positive, and is, of course, proportional to r^2 where r is the droplet radius. Thus, there will be a maximum in ΔG at a radius r* denoted the "critical radius".

The formation of an aerosol particle requires not only that the vapor be supersaturated, but also that spontaneous density fluctuations yield clusters at least as large as the critical embryo. This latter condition leads to an expression for the rate of particle formation. According to Kiang and Stauffer (1973) the nucleation rate for a two component aerosol with vapor phase concentration N_A and N_B if $N_B >> N_A$ is

$$J = 4\pi r^{*2} \beta_A N_B exp(-\Delta G^*/kT)$$

where the starred quantities are evaluated at the critical radius, and β_A is the impinging rate of A molecules. Note that a fundamental requirement for the nucleation of new particles is that all components be supersaturated with respect to the solution. If supersaturation is not achieved, the liquid phase will not be formed. However, even if supersaturation is achieved, the nucleation rate (J) may be so small that the effect is negligible.

We have calculated homogeneous nucleation rates for the formation of sulfuric acid - water solution particles for typical Antarctic and Arctic winter temperature profiles. In the calculations we used temperature profiles taken from the SAM II data set, using cases in which the extinction was many times greater than the background value, indicating the presence of a polar stratospheric cloud. The altitude dependent sulfuric acid vapor concentrations used in our calculations were evaluated for mid-latitude conditions (Hamill et al., 1982). These are reproduced in Table 1. The values are reasonable for the Antarctic before the onset of winter when solar UV radiation is lost and the polar vortex serves as a semi-porous barrier inhibiting the mixing of air from lower latitudes. However, after the stratospheric air mass has cooled and nucleation has taken place, most of the sulfuric acid will be in particulates and the vapor phase concentration will drop to much lower values. Furthermore, the production of sulfuric acid vapor requires photochemical processes which will not take place in the polar night. However, as the sunlight returns in the spring, there may be photochemical production of sulfuric acid in the Antarctic stratosphere. The situation for the Arctic stratosphere is considerably more complicated since the vortex is more asymetrical and air parcels may be exposed to sunlight even in mid-winter. Also, air from lower latitudes may be mixed into the Arctic polar region several times during the course of the winter.

TABLE 1. Gas Phase Sulfuric Acid Concentrations

Altit (km)	$[H_2SO_4]/cm^3$	Altit (Km)	$[H_2SO_4]/cm^3$
10.0	$8.83X10^6$	20.0	$4.21X10^4$
12.0	$5.50X10^6$	22.0	$8.68X10^4$
14.0	$1.01X10^6$	24.0	$1.93X10^5$
16.0	$1.12X10^5$	26.0	$4.59X10^5$
18.0	$3.67X10^4$	28.0	$1.23X10^6$
20.0	$4.21X10^4$	30.0	$2.90X10^6$

Assuming the sulfuric acid vapor concentration varies with altitude as indicated in Table 1 we find the stratospheric nucleation rates presented in Figures 1 and 2. In both of these figures the first panel gives the observed SAM II extinction profile, the second gives the temperature profile for the time and location of the extinction measurement, and the third panel gives the nucleation rate calculated using the temperature profile of the second panel. The nucleation rates were calculated using an arbitrary water vapor content of 5 ppmv. Such a water vapor concentration is perhaps high; late in the season the water vapor content in the Antarctic stratosphere is as low as 2 ppmv. Calculations using the lower value of water vapor pressure yield lower nucleation rates by about one order of magnitude at 20 km and by two orders of magnitude at 27 km. These changes are not significant in view of the extremely large changes in nucleation rate due to variations in temperature. Unlike water vapor, there are no measurements of sulfuric acid vapor concentrations in the winter polar stratosphere. It is likely that sulfuric acid may be highly depleted by growth and sedimentation processes. Decreasing the H_2SO_4 vapor concentration by one order of magnitude leads to decreases of roughly three orders of magnitude in the nucleation rate.

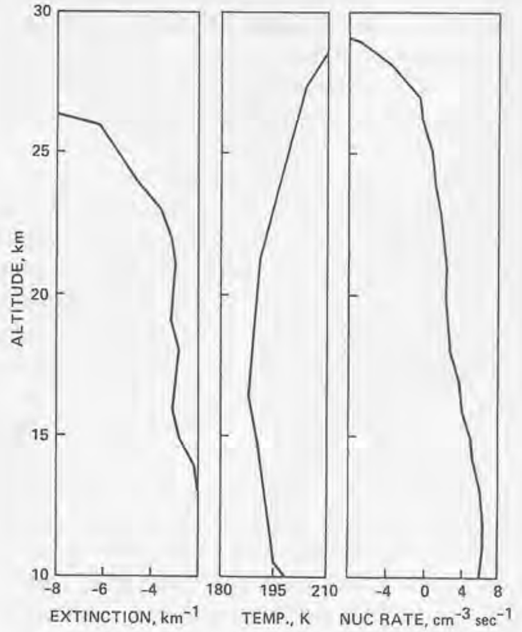

Figure 1. Extinction, temperature, and nucleation rate profiles for a typical Arctic winter PSC event. The extinction and temperature data are taken from the SAM II orbit 51877, Feb 2, 1989.

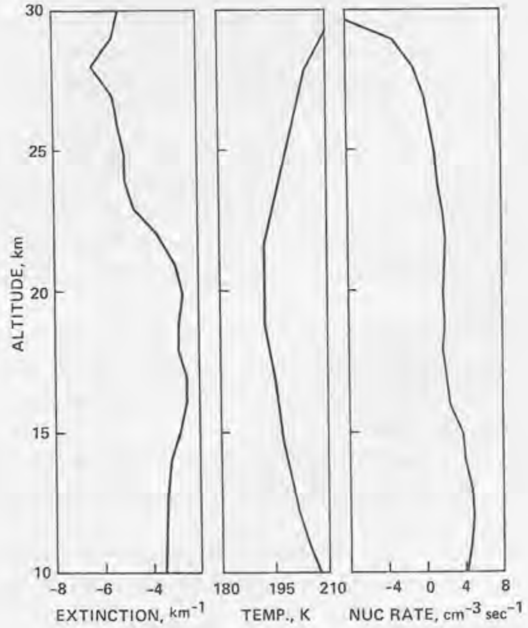

Figure 2. Extinction, temperature, and nucleation rate profiles for a typical Antarctic winter PSC event. The extinction and temperature data are taken from the SAM II orbit 44290, Aug 2, 1987.

Therefore, a removal mechanism for H_2SO_4 will lead to nucleation rates much lower than those presented here.

Note from Figures 1 and 2 that at all altitudes up to 28 or 29 km the homogeneous nucleation rate is far above the "replacement" value of about 10^{-7} to 10^{-8}. The extraordinarily high nucleation rates shown in the figure can not be maintained for they would result in a complete depletion of all the sulfuric acid vapor in a very short time. Furthermore, at lower altitudes the existence of other particles would lead to the depletion of vapor by condensation and of the newly nucleated sulfuric acid droplets by coagulation. Note that even if all of the sulfuric acid vapor were to be incorporated into droplets, this would be an insignificant increase in the aerosol mass.

The extinction and temperature profiles in Figure 1 were taken from the SAM II data set for orbit 51877 on Feb 2, 1989 at 71.55° N at a longitude of 43.72° E. Figure 2 is based on data taken during orbit 44290 on August 2, 1987 over Antarctica at -68.83°S and 46.55°E. In both cases, the polar stratospheric cloud layer extends to about 23 km in altitude, whereas the region of high nucleation rates extends to considerably higher altitudes, beginning to drop off at about 27 km. Therefore, one would expect that above the polar stratospheric clouds, one would find a region of enhanced CN. This agrees with the observation of a high altitude CN layer reported by Hofmann et al.(1989) and Wilson et al. (1989). Furthermore, the results indicate a high nucleation rate inside the polar stratospheric cloud itself. Although this suggests the formation of new CN in this region, the result should be interpreted carefully for several reasons. First of all, the fact that PSC's are present means that there is a significant surface area available and the depletion of sulfuric acid vapor by multi-component particle growth of the PSC's will limit the nucleation rate. Secondly, a burst of nucleation, as might be envisaged when the stratosphere first cools down, would generate a very large number of extremely small particles which would be lost quickly onto the surfaces of the cloud particles. The newly nucleated particles, according to our calculations, will have a radius of only about 0.003 μm and will consequently have a much greater mobility than the PSC particles which were modeled by Toon et al. (1989) and shown to coagulate slowly.

We believe there are two reasons why CN concentrations increase rapidly with altitude. First, below about 25 km the PSC's and pre-existing H_2SO_4 particles will reduce the sulfuric acid vapor by growth and quickly scavenge any newly nucleated (very small) particles. Second, in the mid-latitude stratosphere, H_2SO_4 vapor increases rapidly with altitude due to evaporation of the top of the aerosol layer (Turco et al., 1982; Arnold et al., 1981). As this acid rich air enters the cold polar night and descends into the vortex it will nucleate whenever the temperatures are cold enough. Hence this represents a vapor source at high altitudes. The nucleation at higher altitudes is taking place in very clean air, as evidenced by the SAM II profiles. Therefore, the newly formed particles will coagulate with each other, forming particles large enough to be detected.

Openheimer (1987) suggested that enhanced OH levels led to enhanced production of H_2SO_4 in the polar night. However, the sensitivity of the nucleation rate to low temperatures is so great that we believe the enhanced polar nucleation provides no useful evidence for altered OH levels.

Ternary System Nucleation of HNO_3 - H_2O - H_2SO_4

Recently Jaecker-Voirol et al. (1989) have evaluated the vapor pressures of the nitric acid, sulfuric acid, water ternary system as a function of temperature. They developed a set of equations which would be valid for regular solutions and applied them to this non-regular, highly electrolytic ternary solution. (A regular solution is defined as a mixture which has zero excess entropy of mixing.) They then compared their results with the experimental data obtained by Vandoni (cited in Jaecker-Voirol). Vandoni measured the vapor pressures of HNO_3 and H_2O for the ternary system at 25° C. The close agreement of theory and experiment at this temperature suggested to Jaecker-Voirol and co-workers that one can extrapolate the results to lower temperatures and obtain estimates of the vapor pressures of the three gases over solutions at stratospheric temperatures. Using this formulation, one obtains the vapor pressures for nitric acid, water, and sulfuric acid as functions of temperature and composition. If we assume that the partial pressure of water in the winter polar stratosphere is 4×10^{-4} torr and that the partial pressure of nitric acid vapor is 4 X

10^{-7} torr, then we find that at 195K, there is no composition of a ternary system particle such that there is supersaturation with respect to all components. In fact, the ternary system will not reach supersaturation until the temperature falls below the point at which the frozen binary system HNO_3-H_2O becomes supersaturated. This implies that the binary system would nucleate first, inhibiting the formation of ternary particles. Therefore, we conclude that if the partial pressures of the three components can be extrapolated according to the scheme of Jaecker-Voirol et al., the nucleation of ternary system HNO_3-H_2SO_4-H_2O particles is unlikely. However, it is interesting to note that it is thermodynamically possible to nucleate both binary system HNO_3-H_2SO_4 particles and binary H_2O-H_2SO_4 particles.

Conclusion

We conclude that the homogeneous nucleation of sulfuric acid - water solution particles in the winter polar stratosphere can explain CN observations. The production of new CN is confined to high altitudes because H_2SO_4 vapor levels at low altitudes are depressed by absorption onto pre-existing nitric acid and water ice PSC crystals because any newly nucleated sulfuric acid embryos will be scavenged by pre-existing particles and because a reservoir of H_2SO_4 exists above 30 km. Descent of the high altitude air into the polar vortex will trigger the aerosol nucleation described in this paper. To carry out quantitative evaluations of CN concentrations and size distributions requires a treatment of coagulation and condensation effects, which we plan for later studies.

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