Recent progress in understanding particle nucleation and growth

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SUMMARY

In the past half decade, several new tools have become available for investigating particle nucleation and growth. A number of joint field and laboratory studies exploiting some of these new measurement capabilities will be described and new insights shared. The ability to measure OH, SO₂, H₂SO₄ and aerosol number and size distributions has made possible a comparison between H₂SO₄ production and loss onto particles in continental air masses. In regions remote from urban emissions, agreement is typically quite good. In contrast, joint field measurements of nucleation precursors such as gas phase H₂SO₄ and ultrafine particles suggest that classical bimolecular nucleation theory may not properly describe the tropospheric nucleation process. An alternative mechanism, possibly involving ammonia as a stabilizing agent for H₂SO₄/H₂O molecular clusters is discussed. Finally, ultrafine particle measurements are shown to offer new opportunities for studying particle growth rates. Preliminary results suggest that in a remote continental air mass, gas phase H₂SO₄ uptake is far too slow to explain observed growth rates.

1. INTRODUCTION

For several decades the production and growth of aerosol particles has been thought to be accomplished through the incorporation of oxidation products of reactive sulphur species such as SO₂ and DMS. The mechanism by which particle production and growth occurs and the rate at which this growth takes place, however, remains poorly defined. In order to more fully understand these processes, studies of both the formation of particle precursors and their incorporation into aerosols are required. This paper will review recent progress in our laboratories and discuss its ramifications for understanding particle nucleation and growth. Areas for future investigation will also be proposed.

Particle production and growth begins with the formation of low volatility precursor compounds. Probably the single most important gas phase precursor to particle nucleation and growth, particularly in the marine environment, is sulphuric acid. Sulphuric acid can be formed from the oxidation of SO₂ by the OH radicals and subsequent reactions with O₂ and H₂O. This sequence of reactions is well studied and allows a direct prediction of the H₂SO₄ production rate as a function of SO₂ and OH concentrations. Far more poorly understood are the oxidation products of DMS. Some fraction of DMS which is again initially oxidized by OH results in the production of H₂SO₄. The reaction scheme and the associated rate at which this conversion takes place, however, is essentially unknown. Since H₂SO₄ is not the only product (and under some temperature conditions may not even be a major product) of DMS oxidation, its yield is also unknown. Methane sulphonc acid is also thought to be

a product of DMS oxidation, and is expected to participate in particle growth. Its formation mechanism and yield are poorly known, but are thought to be temperature dependent. Compounds such as DMSO, DMSO₂ and others, are also thought to be important DMS oxidation products with poorly defined yields. Figure 1 shows the probable relation between some of these compounds and particle nucleation and growth. The purpose of this figure is not to describe the mechanism of DMS oxidation; for this, the reader is referred to recent papers by Ravishankara (this issue), Berresheim *et al.* (1995) and Yin *et al.* (1990). Rather, figure 1 places in perspective some of the DMS oxidation products which have been measured by recently developed and highly sensitive techniques that will be briefly reviewed. The role of some of these products, particularly H₂SO₄ in particle nucleation and growth, will also be discussed.

2. ADVANCES IN INSTRUMENTATION

Progress in understanding particle nucleation and growth has long been hampered by a lack of instrumentation capable of measuring the gas phase precursors of these processes and the early particle growth stages themselves. Thus, particle nucleation was studied by measuring reactive sulphur gases such as DMS or SO₂, estimating OH concentrations, calculating H₂SO₄ production rates and then assuming or calculating the amount of H₂SO₄ which was lost to bulk surfaces, existing particles, and the particle nucleation process. Finally, new particles had to grow to > 10 nm diameter (a particle containing about 10⁴ molecules) before they could be efficiently detected

Figure 1. Simplified view of sulphur chemistry in the remote marine atmosphere.

and sized. This left many intermediate steps unmeasured, and under typical remote marine conditions, involved a growth process which is believed to take about a day under full sun conditions to yield a 10 nm particle. In this time period, SO_2 and DMS source compounds can vary substantially, and their oxidation rate by OH by necessity varies by orders of magnitude from day to night, making interpretation even more difficult. In recent years, however, several advances have been made. The hydroxyl radical can now be measured at ambient levels in real time, as can oxidation products thought to be involved in particle nucleation and growth such as H_2SO_4 and MSA. All three of these compounds can, in fact, be measured by a single selected ion chemical ionization mass spectrometer instrument. A simplified drawing of the ground based instrument used to perform such measurements over the past several years is shown in figure 2*a*. Figure 2*b* shows a variation of this instrument used on the NCAR C-130 aircraft in November and December of 1995 to measure these same three compounds during the (Aerosol Characterization Experiment) ACE-I study. Both instruments sample air into a short large diameter inlet in which wall contact is minimal. For the aircraft inlet, extensive physical and chemical wind tunnel tests have shown that there is no detectable mixing of gas from the inlet walls into the central inlet region, even when sampling off-axis flows of up to 24° . The flow tube, ion source, and ion reaction regions are essentially identical in both instruments, and again allow minimal contact between sampled gas and instrument walls. Ions are sampled into a vacuum analysis region through a nitrogen buffer gas and a thin-walled (compared to its diameter) aperture. Ions are then focused and concentrated by electrostatic lenses in a differentially pumped vacuum system and finally analysed and detected by a quadrupole mass spectrometer and channel electron multiplier, respectively. When operating the instrument, air is sampled from the centre of their respective inlets into a flow

tube in which OH radicals are converted into gas phase H_2SO_4 via the following three reactions:

where reaction 1 is typically the rate limiting step (in the lower and mid troposphere) and the rate of OH conversion is controlled by the amount of SO_2 added. To measure OH, isotopically labelled $^{34}\text{SO}_2$ is used at concentrations sufficiently high to ensure that OH is converted into $\text{H}_2^{34}\text{SO}_4$ on a time scale which is short compared to the ambient OH lifetimes.

As a result of the above three reactions, each OH molecule sampled into the flow tube region is titrated into one $\text{H}_2^{34}\text{SO}_4$ molecule. The resulting $\text{H}_2^{34}\text{SO}_4$ is then allowed to react with NO_3^- ions to form $\text{H}^{34}\text{SO}_4^-$ ions:

The HSO_4^- core ions in this reaction can either be derived from OH titration and will thus be detected as $\text{H}^{34}\text{SO}_4^-$ or from ambient atmospheric sulphuric acid and measured as $\text{H}^{34}\text{SO}_4^-$ (for either measurement there is about a 4–5% contribution from the opposite mass sulphur isotope). Thus, both OH and H_2SO_4 concentrations can be measured by the same instrument using the same ion reaction. The mass spectrometer is then used to determine the $\text{HSO}_4^-/\text{NO}_3^-$ core ion ratio which is used to calculate OH and H_2SO_4 concentration. If MSA is substituted for H_2SO_4 in reaction 4, the resulting $\text{CH}_3\text{SO}_3^-/\text{NO}_3^-$ core ion ratio is measured and used in the same way to calculate MSA concentrations.

Figure 2 shows the regions in which the above processes are carried out. The inlet separates and straightens an air stream and constrains its flow velocity. A calibration source which operates under ambient conditions is also contained in the inlet of both

Figure 2. Selected ion chemical ionization mass spectrometer used to measure OH, H_2SO_4 , and MSA. (a) Schematic drawing of ground based instrument showing major instrument details; and (b) aircraft instrument with similar internal structure; only major inlet details are shown.

instruments shown in figure 2. Next, the flow tube region samples air from the centre of the inlet flow. $^{34}\text{SO}_2$ is then added to the sampled air in this region to convert OH into $\text{H}_2^{34}\text{SO}_4$ while ambient H_2SO_4 and MSA simply pass through this region. The H_2SO_4 and MSA subsequently enter the ion reaction region where they are joined by NO_3^- ions which are selectively formed in a separate ionization region. The reagent and product ions leaving this region are forced through an N_2 buffer gas and into a vacuum system where they are analysed. A more detailed discussion of this measurement technique (Eisele & Tanner 1991, 1993; Tanner & Eisele 1995), along with recent measurement results (Eisele *et al.* 1994, 1996), and intercomparison (Eisele *et al.* 1994; Mount *et al.* 1996) results are included elsewhere. In addition, fairly similar but less complex measurement schemes have been developed for other important DMS oxidation products as well, such as DMSO and DMSO_2 (Eisele & Berresheim 1992; Berresheim *et al.* 1993*a,b*). The development of still other gas phase measurement techniques related to particle nucleation and growth is also underway.

While gas phase investigations have moved from the measurement of the raw materials needed for particle nucleation and growth to some of the direct precursors of these processes, particle technology has advanced from detecting particles containing $\geq 10^4$ molecules to detecting particles of $\geq 10^2$ molecules (2.7 nm diameter). At the same time, these ~ 3 nm particles can be measured and sized with far more sensitivity than was previously possible for particles > 10 nm. This is made possible by a recently developed ultra-fine particle instrument.

Ultra-fine particles are detected and sized using a specially designed steady flow condensation nucleus counter (CNC) (Stolzenburg & McMurry 1991). In this instrument the aerosol is saturated with butanol at $\sim 40^\circ\text{C}$ before entering a cylindrical, laminar-flow condenser at $\sim 10^\circ\text{C}$. Heat transfer to the condenser walls leads to cooling of the carrier gas with subsequent supersaturation of the butanol and condensational growth of particles. Particles are grown to $\sim 10\text{--}15\ \mu\text{m}$ diameter so that they can be individually counted and sized optically. Optical detection is achieved using white (halogen) light illumination with forward scattering (Agarwal & Sem 1980). The minimum particle size that can be detected is ~ 2.7 nm.

The butanol supersaturation profile in the condenser varies with radial and axial position. Therefore, a particle's growth is affected by its trajectory through the condenser. We use a sheathed flow arrangement to confine particles to a narrow region close to the axis of the condenser to ensure that they all are exposed to the same butanol supersaturation profile. This ensures that particles of a given initial size all grow to about the same final size.

Ultra-fine particle sizing is achieved with this instrument by utilizing the effect of curvature on vapour pressure (Thompson 1871). As particle size decreases and curvature increases, the butanol saturation ratio that is required to initiate particle growth increases. Because butanol saturation ratios increase with axial position near the condenser inlet, smaller

particles must travel further into the condenser before growth begins. Therefore, smaller particles grow for a shorter period of time and achieve a smaller final droplet size than do larger ones. Useful information on size distributions of particles in the diameter range of *ca.* 3 to 10 nm can be achieved using this approach (Saros *et al.* 1996). For particles larger than *ca.* 10 nm, growth times do not vary sufficiently to permit size discrimination. This measurement approach is ideally suited for the low concentrations of ultra-fine particles that are often encountered in the remote atmosphere.

3. SAMPLE MEASUREMENT RESULTS

Some typical gas phase measurement results from ground based and aircraft investigations are shown in figures 3 and 4 respectively. Figure 3*a* shows OH and H₂SO₄ and MSA concentrations plotted as a function of time of day. Note the clear diurnal variation of OH and, because H₂SO₄ and MSA are formed as a result of OH initiated oxidation, the highly correlated diurnal variation in H₂SO₄ and MSA concentration, as well. Figure 3*b* also shows a similar diurnal variation for DMSO, also resulting from OH oxidation. As shown by figure 3, fast sensitive ground-based measurements of these compounds are now possible and their use in conjunction with other gas phase and particle measurements is proving extremely valuable. Figures 4*a* and *b* show recent aircraft measurements of OH and H₂SO₄ made during the November–December 1995 ACE-I campaign. This figure shows the results of two back-to-back flights which again allows much of the diurnal variation of these compounds to be seen. The aircraft instrument is even more sensitive than its ground-based predecessor and as a result even the 30 s integration time measurements shown provide more than sufficient sensitivity to test photochemistry and particle growth models. MSA was also measured

during ACE-I, but because less than an hour was typically spent at a given altitude, variability was observed to be more dependent on altitude than time of day. Thus, figure 4*c* shows the strong dependence of MSA concentration on the layers of the troposphere being measured. Layers containing MSA concentrations of 10² times that observed in adjacent altitudes was not uncommon. Analysis of the ACE-I data is still in its early stages, and no clear explanation of the data seen in figure 4*c* can be given. It is interesting to speculate, however, that the very high concentrations of gas phase MSA often observed in only a few hundred metre thick layer of the free troposphere might be the remnant of a large bubble of DMS deposited through previous convective activity. Once injected into the free troposphere at a specific altitude, DMS would be initially oxidized by OH over the period of a day or so, producing H₂SO₄, MSA and other unmeasured gas phase products. Many of these products would subsequently interact with existing particles (or in the case of H₂SO₄ it might even produce new particles in this same layer of the free troposphere). The extremely low vapour pressure of H₂SO₄ would, in all probability, result in the near complete uptake of gas phase H₂SO₄ onto particles as will be discussed shortly. MSA, however, is substantially more volatile, particularly at the relatively low H₂O concentration found in the free troposphere, and therefore gas phase MSA might equilibrate with particulate MSA at the vapour pressures shown in figure 4*c*. Since MSA is a fully oxidized product of DMS, there are no further chemical transformations expected to destroy it, either in the gas or aqueous phases. Presumably MSA is eventually removed through rain out. Since gas phase MSA can be measured far more rapidly and sensitively than particulate MSA, it may prove to be a unique tracer for other products of DMS oxidation and also for past convective activity which has deposited DMS far above the boundary layer.

Figure 3. Typical diurnal variation of (a) OH, H₂SO₄, and MSA at Mauna Loa Observatory, Hawaii, and (b) DMSO at Palmer Station, Antarctica.

Figure 4. ACE-I flight measurements of (a) OH plotted as a function of local time and (b) H_2SO_4 plotted as a function of local time, both with an altitude profile included in figure, and (c) MSA plotted as a function of altitude.

4. NEW INSIGHT FROM JOINT GAS PHASE/PARTICLE MEASUREMENTS

(a) *Balancing the production and loss of H_2SO_4*

The major sources and sinks for gas phase H_2SO_4 in a remote measurement site are shown below:

Reaction sequence 5 is reasonably well understood and consists of reactions 1–3. Reaction 7 is not well understood, but its net result is at least quantifiable in terms of an accommodation coefficient and a particle distribution. Reaction sequences 6 and 8, however, are particularly poorly characterized. Thus, an attempt to balance all sources and sinks of H_2SO_4 would prove most difficult. At a remote continental site, however, the concentration of SO_2 is typically much larger than that of DMS, and therefore reaction sequence 6 is expected to make only a minor contribution. Continental air masses are also typically expected to have aerosol concentrations sufficiently high to make H_2SO_4 loss through reaction sequence 7 much larger than through 8. As will be shown in the following section, particle nucleation can occur in continental air masses, but the ultra-fine particles formed have much lower concentrations and surface areas than the residual particles. Thus, in a remote continental site, the

Figure 5. The calculated production and loss of H_2SO_4 plotted as a function of local time for 30 July, 1991. (From Eisele & Tanner 1993.)

production of H_2SO_4 through reaction sequence 5 should be approximately equal to its loss onto existing particles (reaction 7). Since reaction 1 is the rate limiting step in the formation of H_2SO_4 in the troposphere (reactions 1, 2 and 3 requiring days, microseconds, and milliseconds respectively (DeMore *et al.* 1994)), only OH and SO_2 concentrations need to be measured to calculate the H_2SO_4 production rate. These can then be equated with the loss rate for steady state conditions:

$$[\text{OH}][\text{SO}_2]k_1 = [\text{H}_2\text{SO}_4]k_7$$

where k_7 is the rate of loss onto particles. The ability to simultaneously measure all of the above parameters, i.e. OH, SO_2 , H_2SO_4 and particle number and size distribution has, for the first time, made a test of our understanding of H_2SO_4 production and loss possible. Also, fortuitously OH and H_2SO_4 concentrations are found on the opposite side of the above equation. As discussed above these two compounds are measured using the same instrument and reaction scheme, therefore, the relative uncertainties introduced into the above equality by these two measurements is quite small. Unfortunately, however, the SO_2 concentration and the aerosol number density and size distribution measurements probably still introduce about a factor of two uncertainty into this calculation, particularly at low SO_2 concentrations (a commercial Thermal Electron 43S Instrument with a detection limit of 100 pptv was used to measure SO_2 , and particle size and number density were measured with a TSI Model 3071 DMA). Within a factor of two, however, the following tests provided the first real indication of our understanding of H_2SO_4 production and loss. Figure 5 shows the comparison between calculated production and loss of H_2SO_4 for H_2SO_4 accommodation coefficients of 0.5 and 1.0. The data used for this calculation were measured as part of a 1991 OH intercomparison/photochemistry study in a remote Rocky Mountain location near Boulder, Colorado. As seen from figure 5, agreement is quite good (particularly using an accommodation coefficient of 0.5), except during night-time and early morning measurements. At these times, SO_2 is near the detection limit and H_2SO_4 concentrations are so low that re-evaporation from the aerosol may become significant.

Figure 6. Measured and calculated H_2SO_4 concentrations plotted as a function of local time for (a) continental and (b) midoceanic sites.

Similar results were obtained on other relatively unpolluted days and are discussed in more detail in a previous paper by Eisele & Tanner (1993). Under highly polluted conditions, discrepancies of more than an order of magnitude were common.

In 1993, the Tropospheric OH Photochemistry Study brought together the same set of instruments at a similar location except that aerosol size and number density were measured using a University of Minnesota DMA that is similar in design to the TSI Model 3071. Figure 6a shows a comparison between measured H_2SO_4 concentrations and those calculated using measured OH and SO_2 concentrations, aerosol size and number distribution, and assuming an accommodation coefficient of 1.0. These same measurements were also performed at Mauna Loa Observatory in Hawaii in 1992; these results are plotted in figure 6b in the same format used in figure 6a. In both cases, agreement is often seen to be better than a factor of two, but this time using an accommodation coefficient of 1.0 (Weber, personal communication).

Recently, another joint study, this time in our laboratory, attempted to measure the accommodation coefficient of H_2SO_4 on both ammonium sulphate and sodium chloride particles. Though only preliminary results are presently available, an accommodation coefficient between 0.5 and 1.0 appears likely on both particle surfaces.

The relatively good overall agreement both in the variability and absolute value of calculated H_2SO_4 production and loss provides hope that this same approach might be applicable in estimating H_2SO_4

Figure 7. The flux of particles through the 3–4 nm size range as a function of H_2SO_4 concentration for (a) Mauna Loa and (b) Colorado. (From Weber *et al.* 1996.)

production from DMS (if SO_2 sources can be accounted for using the above method). Data from the recently completed ACE-I campaign presently provide an ideal opportunity to test these ideas, offering far more sensitive SO_2 and DMS measurements, multiple DMA measurements, and more sensitive OH and H_2SO_4 measurements.

(b) Particle nucleation

While the previous discussion of H_2SO_4 uptake by particles tends to support classical understanding of particle growth, recent nucleation studies are suggesting mechanisms quite different from classic bimolecular nucleation theory. By making simultaneous measurements of gas phase H_2SO_4 and ultra-fine particles, it was quickly determined that, as expected, these two parameters were closely correlated. The concentration of ultra-fine particles, however, depends both on production (as shown by reaction sequence 8) and loss onto existing particle surfaces. Therefore it is not the concentration of ultra-fine particles but rather only their rate of production that should depend on H_2SO_4 concentration directly.

Figures 7a and b show the calculated flux (J) of ultra-fine particles passing through the 3–4 nm diameter size range as a function of the H_2SO_4 concentration at the Mauna Loa and Colorado measurement sites respectively. Both plots show a compilation of all relevant data obtained during the campaigns, and J was calculated from the measured particle distribution function and by assuming an H_2SO_4 accommodation coefficient of 1.0 for ultra-fine

Figure 8. The vapour pressure of H_2SO_4 as a function of relative humidity for several ammonia/sulphate ratios from 0 to 2. (From Marti *et al.* 1997.)

growth (Weber *et al.* 1996). Since 3–4 nm is the smallest size range of particles that can be measured, the flux through this size range presently provides the best estimate of nucleation rate. Also, however, because nucleating particles can be lost onto varying concentrations of larger particles prior to being detected in the 3–4 nm range, it is assumed that the highest calculated fluxes best characterize the actual nucleation rate. If a line is drawn approximately through these high flux points in both figures 7a and b, its slope in both cases appears to be about 2. This suggests a nucleation rate which varies approximately as the square of the H_2SO_4 concentration. This is in sharp contrast to the far more vertical lines showing classical nucleation theory predictions. Present results suggest a far weaker functional dependence on H_2SO_4 and also that nucleation can occur at a much lower absolute concentration of H_2SO_4 than predicted by classical theory. If an accommodation coefficient of 0.5 were assumed in the calculation of j , the slope of the maximum flux lines would remain the same (2) and the J values would only drop by a factor of two. These calculations are discussed in more detail by Weber *et al.* (1996).

The large disparity between classical bimolecular nucleation theory and the present results requires a re-evaluation of the use of this theory for describing nucleation in the troposphere or at least the lower troposphere where the present measurements were performed. To pose this issue in a different way: why, in hindsight, would molecular clusters of H_2SO_4 and H_2O not be expected to react with basic compounds such as NH_3 ? NH_3 is typically more abundant than gas phase H_2SO_4 , it is highly soluble, and is commonly found along with H_2SO_4 in larger particles. If NH_3 were to react with a molecular cluster containing nucleation precursors such as H_2SO_4 and H_2O , it could form ammonium bisulphate or even ammonium sulphate. This might well reduce the vapour pressure or the loss rate of H_2SO_4 from these clusters. If this were to occur, the ammonia could have a significant effect on the nucleation process such as that shown in figure 7.

Figure 9. A compilation of (a) H_2SO_4 and (b) ultrafine concentrations plotted as a function of local time. The solid line shows the average clear day solar flux intensity. Note the near immediate rise of H_2SO_4 with sunlight and the 1–2 hour delayed response of ultrafines.

(c) H_2SO_4 vapour pressure

To investigate this possibility, joint laboratory studies were conducted to measure the vapour pressure of H_2SO_4 above aerosols containing various mixtures of H_2SO_4 and NH_3 . Figure 8 shows the results of these studies for several different ratios of NH_3 to H_2SO_4 from 0 to 2. In each case, the H_2SO_4 vapour pressure is plotted as a function of relative humidity. For pure H_2SO_4 the vapour pressure is compared to that calculated by Ayers *et al.* (1980), and agreement is seen to be reasonably good. As the ammonium content of the particles is increased to 13, 15 or 33 %, the vapour pressure of H_2SO_4 appears to drop slightly. However, when ammonia concentration reaches 80 % of H_2SO_4 , the drop becomes very pronounced. When the average composition of ammonium bisulphate is reached, the vapour pressure of H_2SO_4 is reduced by two to three orders of magnitude, depending on relative humidity. To a crude approximation, this dependence on ammonia content suggests that each ammonia molecule dramatically reduces the ability of one sulphuric acid molecule to leave the particle with the excess acid molecules loss largely unimpeded. At still higher ammonium/sulphate ratios (2) the H_2SO_4 vapour pressure drops so low that it is difficult to measure. While the H_2SO_4 vapour pressure above ammonium sulphate is very low, the vapour pressure of ammonia

is probably quite high (Stelson 1995). It is therefore less likely that ambient NH_3 concentrations will be sufficiently high such that ammonium sulphate molecular clusters will play an important role in atmospheric nucleation (though little quantitative information can be included about ammonia vapour pressures until additional measurements are made). The two to three order of magnitude reduction in H_2SO_4 vapour pressures for the ratio of 1:1 shown in figure 8 is, however, already sufficient to dramatically alter calculated nucleation rates if this same vapour pressure dependence applies to molecular clusters/ultra-fine particles.

In attempting to understand how NH_3 -stabilized molecular clusters might grow into particles, one must also briefly examine the role that statistics might play in this process. For the large particles shown in figure 8 (10^2 nm diameter) ammonium content is listed in fractional concentrations. However, for small molecular clusters with only a few H_2SO_4 molecules, there is presumably a probability distribution for having 1, 2, 3, ... ammonia molecules associated with each cluster. If the molecular cluster of interest has no ammonia molecules, or perhaps only one ammonia molecule compared to two or three sulphuric acid molecules, then from the predictions of classical theory shown in figure 7, it probably has essentially no possibility of growth for the H_2SO_4 concentrations

typically measured. However, even if the average $\text{NH}_3/\text{H}_2\text{SO}_4$ concentration ratio is well below one, there will still be some significant fraction of molecular clusters containing, for example, two H_2SO_4 molecules and two NH_3 molecules. If the results shown in figure 8 can be applied to molecular cluster growth, a reduction in H_2SO_4 loss by several orders of magnitude might well make the further growth of the latter cluster probable. While highly speculative, a scenario such as this could explain the present results, which suggest a kinetically controlled process depending on $[\text{H}_2\text{SO}_4]^2$ and, at the same time, predict a nucleation rate which is many orders of magnitude slower than that calculated for H_2SO_4 uptake at the collision rate. It is also interesting to note that the calculated J values in figure 7*b* are somewhat higher than in figure 7*a*, and the ammonia concentrations are also expected to be much higher over the continent than at Mauna Loa (Langford *et al.* 1992; Tanner & Eisele 1991).

(d) Ultra-fine growth rates

Small particles (particle diameter $\ll$ mean free path) are typically assumed to grow at a constant diameter growth rate, independent of their size, i.e. they incorporate molecules at a rate which is proportional to their surface area. The most conspicuous growth thus occurs when aerosols are smallest. If nucleation is assumed to begin with a cluster of just a few H_2SO_4 , H_2O , and maybe some NH_3 molecules, then the initial size of this nucleating particle is *ca.* 1 nm. It need then only grow an additional 2 nm in diameter before it can be detected as a particle. Small ultra-fine particles therefore offer a unique opportunity to study early stages of growth. Since the nucleation process requires the presence of relatively high H_2SO_4 concentrations, it is expected to have at least as strong a diurnal variation as H_2SO_4 and probably stronger ($[\text{H}_2\text{SO}_4]^2$). Thus, the time between sunrise and the appearance of the first ultra-fines provides a measure of the approximate time required for growth into the 3–4 nm range or *ca.* 2 nm of growth, under the ambient conditions for which the observations were made. Figure 9*a* shows a compilation of all the H_2SO_4 data and the average clear sky solar fluxes plotted as a function of time of day for the previously discussed 1993 Colorado measurements. Note the close correspondence between the rise of solar flux and H_2SO_4 concentration. Unfortunately, afternoons and evenings were often cloudy and/or rainy and therefore H_2SO_4 values did not decrease with clear sky solar flux. Figure 9*b* shows a similar plot for ultra-fine particles. These do not begin to rise at sunrise with H_2SO_4 . Rather, they change little until one or two hours after H_2SO_4 has risen. Using this rise time, a growth rate in diameter of 1–2 nm h⁻¹ is estimated for ultra-fine particles at this site. Maybe a slightly better estimate of growth rate would be obtained by assuming that on average the nucleation process begins when the average H_2SO_4 concentrations shown in figure 7*a* are reached. This would suggest growth rates closer to 2 nm h⁻¹. Interestingly, this rapid growth rate can not be obtained by the incorporation of H_2SO_4 , H_2O or even NH_3 alone. This

observed growth rate is about an order of magnitude larger than can be explained by H_2SO_4 incorporation, even with an accommodation coefficient of one. Though the data were more scattered at the MLOPEX II study and probably more dominated by transport, this large disparity between observed and calculated H_2SO_4 induced growth did not arise. At present, the most likely explanation for this very rapid observed growth rate is that other low volatility compounds are contributing to the growth process. Since this disparity appears very large only in continental air masses, very large or highly polar hydrocarbons would seem likely candidates to account for this rapid growth.

5. CONCLUSIONS

Recently developed instrumentation is opening up exciting new avenues for investigating particle nucleation and growth. In the absence of significant DMS and particle nucleation, H_2SO_4 production and loss can be reasonably well-characterized and balanced. This offers hope that the production rate of H_2SO_4 from DMS might also be quantifiable in the near future. The application of classical nucleation theory in the troposphere has been questioned, and a more kinetically controlled process, possibly involving NH_3 , is posed as a possible alternative. The results of ACE-I which included NH_3 measurements along with those of H_2SO_4 , H_2O and ultra-fines are expected to substantially improve present understanding in this area. If the results shown in figure 7 represent tropospheric nucleation in general, then nucleation events may be far more prevalent and important than present models would suggest. Finally, the measurement of small, size selected, ultra-fine particles now opens up the possibility of studying particle growth processes on a time-scale which is short compared to a day. This is extremely important, because particle growth precursors and dynamics both vary substantially over the time period of a day. Thus, attempting to understand an already highly complex process with multiple varying parameters is particularly difficult. The ability to determine growth over the period of an hour or two under relatively stable chemical and dynamic conditions, however, offers far more hope of obtaining a detailed understanding of this process over the next decade.

A great deal of new insight into particle nucleation and growth has been gained by this group and others over the past half decade and far more progress is anticipated in the near future. Some of the areas in which this progress is desired and anticipated are: understanding DMS oxidation and the subsequent yield of H_2SO_4 and MSA; quantifying the role of NH_3 in particle nucleation; being able to accurately predict nucleation events from precursor or even source gas measurements; and understanding and quantifying the role of hydrocarbons in aerosol growth.

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Discussion

B. A. THRUSH (*University of Cambridge, UK*). You suggested that the rate of formation of ultra-fine particles in the early morning could be explained by the incorporation of organic molecules which are much more abundant than sulphuric acid. Could the nuclei for formation of the particles be cluster ions, since the attractive forces between ions and polar molecules greatly enhance the collision rate?

F. L. EISELE. Atmospheric ion concentrations do not in general rise during the daylight hours. Continental ground level tropospheric ions are typically formed about 20% from cosmic rays and 80% from radon gas. Thus, reduced convection at night often results in an increase in ion concentration at night rather than the day due to increases in radon concentrations closer to the ground at night. Ambient ion concentrations ($10^2\text{--}10^3\text{ cm}^{-3}$) are also not sufficient to account for the observed growth rates, assuming typical ion–molecule reaction rates of $10^{-9}\text{ cm}^3\text{ s}^{-1}$ or even assuming ion–ion recombination rates of $10^{-6}\text{ cm}^3\text{ s}^{-1}$. Also the total number of ions produced per second (about 10 cm^{-3}), if distributed uniformly on all particle surfaces, could not account for the observed ultra-fine particle growth. The production rate of ions, however, is more than sufficient to account for the rate of nucleation of new particles (10^1 s^{-1} and 10^{-2} s^{-1} respectively). Either ions or their recombination products (some of which are probably hydrated ammonium bisulphate clusters formed from the recombination of $\text{NH}_4^+(\text{H}_2\text{O})_n$ and $\text{HSO}_4^-(\text{H}_2\text{O})_m$ ions) might form relatively stable molecular clusters that might compete with or dominate over neutral sulphate or ammonium sulphate cluster formation rates. This is an area that we are just beginning to investigate.

R. A. COX (*University of Cambridge, UK*). What is the role of N_2 collisions with the nucleating embryo?

F. L. EISELE. The N_2 shown in my nucleation figure was simply intended to show that classical nucleation is considered to involve a competition between a clustering rate of H_2SO_4 and H_2O molecules and their collisionally induced thermal decomposition rate (with N_2 as a common collision partner).

R. A. COX. Is the thermal energy release influencing the nucleation process at any stage?

F. L. EISELE. It would seem unlikely that the energy released in the cluster growth process itself would affect nucleation other than in determining if the initial molecular cluster

could be formed. Once a cluster contains several molecules, the energy introduced by an additional H_2SO_4 molecule being added will be shared by the molecules within the cluster. It is therefore unlikely that the energy available to any individual H_2SO_4 molecule would be sufficient to eject that H_2SO_4 molecule. If an H_2O molecule is lost, it will probably be regained shortly to maintain an optimal $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ratio. Since H_2SO_4 concentrations are typically low and growth rates of ultra-fine particles appear to be of the order of one H_2SO_4 molecule each 10–100 s, thermalization of the nucleating clusters between successive additions of H_2SO_4 and H_2O molecules would seem likely.

R. S. SCORER (*London, UK*). What do you mean by ‘clean’ continental air? In my experience there is no continental air (except possibly over snow and ice) in which there is a deficiency of cloud condensation nuclei so that cloud particle condensation always begins at (i.e. only very slightly over) water saturation. What I have in mind is that over the ocean we occasionally find air deficient in condensation nuclei, but never in air that has recently been over land.

F. L. EISELE. Clean continental air is, of course, a relative term, and I was using it to refer to an air mass which had not recently been (within the past day or few days) influenced by urban emissions: i.e. air that has travelled largely over unpopulated areas for the past 1000 km. I agree that we would not expect to find continental air which is deficient in CCN or CN. Instead, I would argue that the constant presence of significant CN and CCN surface area allows us to

assume that most gas phase H_2SO_4 is lost by uptake onto existing particles as opposed to the production of new particles. This assumption is then used to calculate and compare H_2SO_4 production and loss. In air masses containing large anthropogenic contributions $> 10^4 \text{ CN cm}^{-3}$ and NO_x in the ppb range, the calculated H_2SO_4 production and loss do not agree, as they did in the more remote continental air masses.

P. S. LISS (*University of East Anglia, UK*). The proposed importance of ammonia in the particle growth is very interesting, particularly in the context of the remote marine atmosphere. You stressed the potential importance of ammonia in reducing the volatility of sulphuric acid microdroplets, so encouraging their growth. Over the oceans remote from land it is notable that aerosols have $\text{NH}_4^+/\text{NSSS}$ ratios of order unity in molar units. Further, the emission fluxes of both NH_3 and DMS from the oceans also appear to be in approximately a 1:1 molar ratio. These observations support your hypothesis that ammonia may be important for the growth of aerosol particles in the marine atmosphere.

F. L. EISELE. I would agree that the ocean might well supply both sulphur and ammonia for the aerosol nucleation and growth process. I do not know the ratio of DMS/ammonia emissions, but measurements of their average value and variability would both be of considerable interest. Our present research effort, however, is more focused on understanding the nucleation process itself.