Nucleation rate of particles in the lower atmosphere: Estimated time needed to reach pseudo-steady state and sensitivity to H_2SO_4 gas concentration

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[1] Using a kinetic model, we estimate the time-needed (t_0) to establish a pseudo-steady state nucleation when sulfuric acid concentration ([H_2SO_4]) suddenly increases to a certain fixed level. We find that t_0 is roughly inversely proportional to [H_2SO_4]. The assumption of instantaneously achieved pseudo-steady state concentration of critical clusters, on which the classical nucleation theories are based, is no longer valid when t_0 is longer than the time period that [H_2SO_4] can be treated as constant. Under the lower marine atmospheric conditions considered in this study, the nucleation rate predicted by ion-mediated nucleation theory is very sensitive to [H_2SO_4] when [H_2SO_4] is low ($<\sim 7 \times 10^6$/cm^3) but such a sensitivity reduces significantly as [H_2SO_4] increases, which is quite different from that predicted with classical binary and ternary homogeneous nucleation theories.   INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere— composition and chemistry. **Citation:** Yu, F., Nucleation rate of particles in the lower atmosphere: Estimated time needed to reach pseudo-steady state and sensitivity to H_2SO_4 gas concentration, *Geophys. Res. Lett.*, *30*(10), 1526, doi:10.1029/2003GL017084, 2003.

1. Introduction

[2] Despite intensive research over last several decades, the fundamental mechanism that leads to the ubiquitous background of ultrafine aerosols in the atmosphere remains poorly understood. Binary homogeneous nucleation (BHN) of H_2SO_4 and H_2O has generally been presumed to be the principal particle formation mechanism. The difficulty of BHN theory in explaining the particle formation observed recently in the lower troposphere implies that mechanisms other than BHN may be responsible for the observed nucleation events [e.g, *Weber et al*, 1996; *Clarke et al.*, 1998]. Ternary homogeneous nucleation (THN) theory involving H_2SO_4-H_2O-NH_3 [e.g., *Coffman and Hegg*, 1995; *Korhonen et al.*, 1999; *Ball et al.*, 1999; *Napari et al.*, 2002] and ion-mediated nucleation (IMN) involving H_2SO_4-H_2O-Ion [*Yu and Turco*, 2000] have been proposed as the alternative particle formation mechanisms.

[3] Based on THN theory, ammonia stabilizes the critical embryo (reducing its size) and thus dramatically increases the nucleation rate. According to IMN theory, the charged molecular clusters, formed around air ions, are much more stable and can grow significantly faster than corresponding neutral clusters, and thus can preferentially achieve stable, observable sizes [*Yu and Turco*, 2000, 2001]. One of major differences between IMN theory and classical nucleation theories is that, at a given sulfuric acid gas concentration ([H_2SO_4]), IMN theory considers kinetically how clusters of various sizes evolve starting at monomers while classical theories assumes an instantaneous pseudo-steady state concentration of critical embryos. [H_2SO_4] usually changes rapidly during the nucleation events, and question concerning the validity of instantaneous pseudo-steady state assumption has been raised [*Yu and Turco*, 2001].

[4] While both THN and IMN theories introduce new specie into the nucleation system (NH_3 and ions, respectively), H_2SO_4 still is the key nucleating specie. In this paper, we study the sensitivity of nucleation rate to [H_2SO_4]. The time-needed to establish the pseudo-steady state nucleation when [H_2SO_4] suddenly increases to a certain level is also investigated. Our emphasis is on IMN theory but comparisons with BHN and THN theories are made.

2. IMN Theory and Kinetic Model

[5] The particle nucleation is essentially the result of several competing dynamic processes of molecular clusters: clustering growth, evaporation shrink, and scavenging by pre-existing particles. In the atmosphere, the clustering among hydrated H_2SO_4 gas molecules leads to the formation and growth of various clusters. Those clusters that survive the evaporation/scavenging and grow to stable sizes are considered nucleated particles. Under typical conditions in the lower atmosphere where nucleation events have been observed, neutral sub-critical H_2SO_4-H_2O clusters are very unstable and evaporate quickly back to monomers.

[6] Both H_2SO_4-H_2O-NH_3 and H_2SO_4-H_2O-Ion clusters are believed to be much more stable than neutral H_2SO_4-H_2O clusters. In addition, H_2SO_4-H_2O-Ion clusters grow much faster than the neutral ones as a result of electrical interactions of polar molecules with ions [*Yu and Turco*, 2000, 2001]. The charged clusters lose these advantages (enhanced stability and growth rate) when they are neutralized by ions of opposite sign. The dynamic interactions among gas molecules and clusters of both charged and neutral are the essentials of IMN theory and only a kinetic model can simulate these processes properly [*Yu and Turco*, 2001].

[7] We employ an advanced particle microphysics model that simulates a size-resolved multicomponent aerosol system via a unified collisional mechanism involving both neutral and charged particles down to molecular sizes [*Yu*

and Turco, 2001]. The size-resolved ion-ion recombination coefficients, ion-neutral collision kernels, and neutral-neutral interaction coefficients calculated in the model are physically consistent and depend on ambient conditions [*Yu and Turco*, 2001]. Due to the lack of the information about the evaporation coefficients of small clusters, a simple adjustment to the accommodation coefficient was assumed as an expedient means of parameterizing the evaporation process in our earlier model [*Yu and Turco*, 2001]. In the current model, the evaporation equations [*Yu and Turco*, 2001] are solved explicitly, with the evaporation coefficients of neutral H_2SO_4-H_2O clusters calculated based on the assumption that the escape frequency of H_2SO_4 molecules equals the collision frequency when the cluster is in equilibrium with the surrounding H_2SO_4 molecules. Nevertheless, for the marine boundary conditions studied here, two different approaches (to treat the evaporation process) give similar results as both approaches indicate that the growth of neutral sub-critical clusters is too slow to lead to any nucleation. The scheme to calculate enhancement factors for the interactions rates of H_2SO_4 molecules with ions/charged particles has been updated with a recently derived analytical expression which gives the enhancement factor as a function of the size of the charged particles, the size and dipole moment of condensable vapor molecules, and ambient temperature [*Nadykto and Yu*, 2003].

[8] It is noteworthy that IMN theory is different from the classical ion-nucleation (INU) theory [e.g., *Hamill et al.*, 1982; *Raes et al.*, 1986]. Classical "ion-nucleation" modifies the free energy needed to form critical embryos (similar to THN) by considering the Thomson effect, but does not consider how the pseudo-steady state distribution of clusters is established. Most importantly, the effect of charge on the growth rate of clusters, which is critical, is not considered.

[9] At a given condition, the classical nucleation theories (BHN, THN, INU) predict the nucleation rate from formulas assuming a pseudo-steady state concentration of critical embryos. On the contrast, the kinetic model on which the IMN theory is based explicitly simulates the evolution of cluster distributions. From these varying cluster distributions (dN/dD_p), an equivalent IMN theory-predicted nucleation rate ($J_{D_0}^{IMN}$) of particles with diameter D_0 can be calculated as the following,

$$J_{D_0}^{IMN} = \left.\frac{dN}{dD_p}\right|_{D_0} \cdot \left.\frac{dD_p}{dt}\right|_{D_0} = \left.\frac{dN}{dD_p}\right|_{D_0} \cdot 2v_1 \cdot \frac{[H_2SO_4]}{4} \cdot \bar{c} \quad (1)$$

where $\bar{c}$ is the mean thermal speed of the condensing hydrated H_2SO_4 monomers, and v_1 is the amount that particle volume increases upon the addition of a single H_2SO_4 molecule (and associated H_2O molecules to maintain phase equilibrium). Two values of D_0 are considered here: diameter of critical embryo (D_{crit}) and 3 nm. Equation (1) is the same as the formula *Weber et al.* [1996] used to estimate observed nucleation rates (J_{3nm}^{obs}) from the measured $[H_2SO_4]$ and particle size distributions down to 3 nm.

3. Simulations

[10] We consider two different ambient conditions corresponding to two different nucleation events observed: one in the tropical marine boundary layer [*Clarke et al.*, 1998, — Case1] and the other at a remote marine site [Mauna Loa

Observatory, *Weber et al.*, 1996, — Case 2]. The mean values of temperature (T), relative humidity (RH), and pre-existing particle surface area (S_0) are 25°C, 95%, 10 $\mu m^2/cm^3$, respectively for case 1 and are 8°C, 48%, 50 $\mu m^2/cm^3$, respectively for case 2. Based on the locations of the measurement sites, we choose an ionization rate (Q) of 2 and 5 ion-pairs/cm^3s [*Reiter*, 1992] for case 1 and case 2, respectively. Two additional ionization rates are considered for sensitivity study (5 and 10 ion-pairs/cm^3s for case 1; 2 and 10 ion-pairs/cm^3s for case 2).

[11] Three types of particles (neutral, positively charged, and negatively charged) are treated in the model. All particles are assumed to be composed of H_2SO_4 and H_2O and the water contents of clusters/particles are calculated based on thermodynamic equilibrium. We initialized our model with neutral monomers (i.e, hydrated H_2SO_4 gas molecules) and the ambient particles corresponding to the surface area given above. At $t = 0$ minute, only monomers and ambient particles exist. As time passes by, monomers aggregate into clusters of various sizes. Our model keeps track the evolution (growth, neutralization, evaporation, scavenging, etc) of the size distributions of both charged and neutral clusters/particles. From these size distributions, the nucleation rates are calculated with equation (1).

3.1. Estimated Time Needed to Achieve Pseudo-Steady State

[12] Figure 1 shows the variations of $J_{D_{crit}}^{IMN}$ (solid lines) and J_{3nm}^{IMN} (dot-dashed lines) with time at 4 different values of $[H_2SO_4]$: (a) case 1, and (b) case 2. We run the model for three hours and the value of $[H_2SO_4]$ for each run is indicated along each line. T, RH, Q, and $[H_2SO_4]$ are fixed during each 3-hour simulation. The diameter of critical embryo (D_{crit}, calculated with classical nucleation theory) increases as $[H_2SO_4]$ decreases. The values of $J_{D_{crit}}^{IMN}$ are calculated at a specific D_{crit} corresponding to each $[H_2SO_4]$. As expected, $J = 0/cm^3$s at the beginning since no clusters of stable sizes have formed yet. The nucleation rates increase quickly as clusters begin to form and reach relative stable values (i.e, pseudo-steady state) after a certain period of time (t_0). t_0 can be defined as the time when the relative change of nucleation rate becomes smaller than certain value ε_0 for the first time,

$$\left.\frac{1}{J_D^{IMN}}\frac{dJ_D^{IMN}}{dt}\right|_{t_0} < \varepsilon_0 \quad (2)$$

[13] We choose $\varepsilon_0 = 0.6\%$ min^{-1}, and the position of t_0 in each line is also indicated in Figure 1 (filled circles for $J_{D_{crit}}^{IMN}$ and opaque circles for J_{3nm}^{IMN}). An ε_0 value of 0.6% gives visually reasonable locations of t_0 in the curves shown in Figure 1 that separate the regions with rapid change in nucleation rate and regions with stable nucleation rate.

[14] The nucleation system achieves pseudo-steady state (with regard to formation rate of particles with diameters D_{crit} and 3nm) quickly when $[H_2SO_4]$ is high. For the two cases considered in this study, t_0 for $J_{D_{crit}}^{IMN}$ is ≤5 minutes and for J_{3nm}^{IMN} is ≤15 minutes at $[H_2SO_4]$ of 5 × $10^7/cm^3$. Note that the slight decrease in nucleation rates after t_0 at $[H_2SO_4]$ of 5 × $10^7/cm^3$ is due to the scavenging of sub-nucleated clusters by nucleated particles. t_0 is almost inversely proportional to $[H_2SO_4]$. When $[H_2SO_4]$ = 1 ×
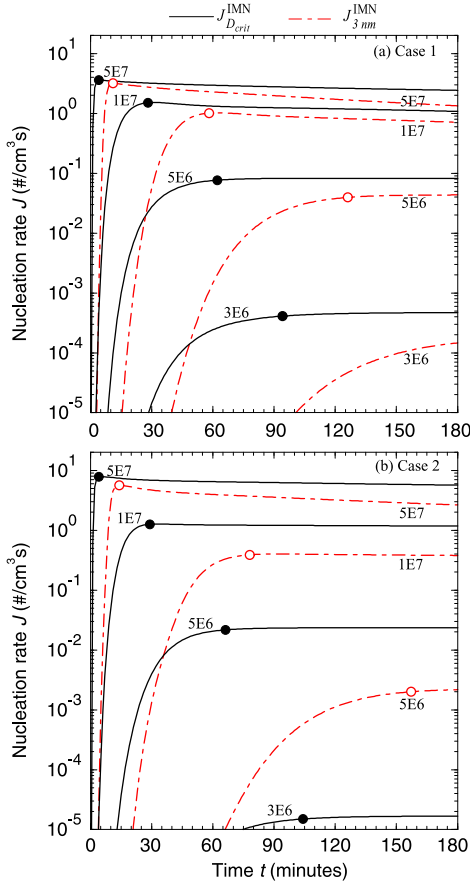
Figure 1. The variations of model calculated $J_{D_{crit}}^{IMN}$ (solid lines) and J_{3nm}^{IMN} (dot-dashed lines) with time at 4 different values of $[H_2SO_4]$: (a) case 1 ($T = 25°C$, $RH = 95\%$, $S_0 = 10$ μm^2/cm^3, $Q = 2$ ion-pairs/cm^{3}s), and (b) case 2 ($T = 8°C$, $RH = 48\%$, $S_0 = 50$ μm^2/cm^3, $Q = 5$ ion-pairs/cm^{3}s). The value of $[H_2SO_4]$ for each run is indicated along each line. T, RH, Q, and $[H_2SO_4]$ are fixed during each 3-hour simulation. The corresponding values of time needed to established pseudo-steady state nucleation are also indicated.

10^7/cm^3, t_0 is $\sim$ half hour for $J_{D_{crit}}^{IMN}$ and $\sim$ one hour for J_{3nm}^{IMN}.

[15] In our simulations, we assume that $[H_2SO_4]$ is constant. In the real atmosphere where significant nucleation has been observed, $[H_2SO_4]$ typically increases rapidly and then decreases quickly [e.g., *Weber et al.*, 1996; *Clarke et al.*, 1998]. There exit a phase lag between the peak in $[H_2SO_4]$ and peak concentration of measurable newly formed nanoparticles (down to 3 nm). The time of this delay is consistent with t_0 shown in Figure 1. Note that t_0 shown above are based on IMN theory that has taken into account the enhanced growth rate of charged clusters. Without such enhancement (as in the cases of THN and BHN), t_0 are expected to be larger. For relative low values of $[H_2SO_4]$ ($< \sim 1 \times 10^7$/cm^3) and when $[H_2SO_4]$ changes rapidly, t_0 may be much bigger than the time period that $[H_2SO_4]$ can be treated as constant. Under such conditions, the assumption that pseudo-steady state concentration of critical clusters is achieved instantaneously following the

changes of $[H_2SO_4]$, which is a key assumption of classical nucleation theories, is no longer valid.

[16] Figure 1 also indicates that J_{3nm}^{IMN} are a factor of $2-10$ smaller than $J_{D_{crit}}^{IMN}$. The difference is due to the scavenging of nucleated clusters by pre-existing particles before they grow to 3 nm.

3.2. Sensitivity of Nucleation Rate to Sulfuric Acid Concentration

[17] Since nucleation rate is very sensitive to t when $t < t_0$, we compare $J_{D_{crit}}^{IMN}$ at $t = 180$ minutes to make sure that pseudo-steady states have been reached under the conditions. Figure 2 describes the dependence of pseudo-steady state nucleation rate $J_{D_{crit}}^{IMN}$ on $[H_2SO_4]$ at three ionization rates ($Q = 2, 5, 10$ ion-pairs/cm^{3}s). The nucleation rates predicted with classical BHN theory (J^{BHN}) and THN theory at two NH$_3$ concentrations (J^{THN}) are also shown for comparison. J^{THN} is calculated from the parameterization given by *Napari et al.* [2002]. J^{BHN} are extremely small under the conditions and have been scaled by a factor of 10^{10} to be displayed in the same plot. Both THN and IMN theories can predict significant nucleation under the
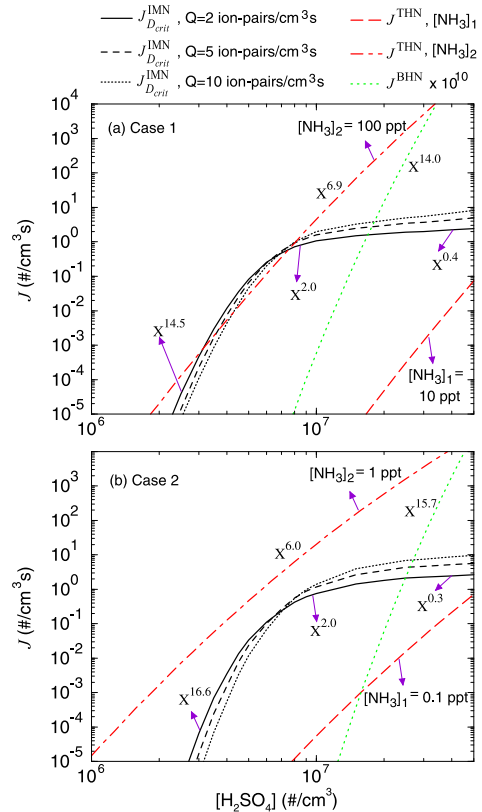

Figure 2. The dependence of pseudo-steady state nucleation rate $J_{D_{crit}}^{IMN}$ on $[H_2SO_4]$ at three ionization rates ($Q = 2, 5, 10$ ion-pairs/cm^{3}s) for (a) case1 and (b) case 2. The nucleation rates predicted with classical BHN theory (J^{BHN}) and THN theory at two NH$_3$ concentrations (J^{THN}, based on parameterization given by *Napari et al.*, 2002) are also shown for comparison. Note that J^{BHN} have been scaled by a factor of 10^{10}. The sensitivity of nucleation rates to $[H_2SO_4]$ can be seen from the values of α in the relation $J \propto X^{\alpha}$ where $X = [H_2SO_4]$.

conditions considered. J^{THN} is very sensitive to NH_3 concentration ($[NH_3]$). A factor of 10 increase in $[NH_3]$ enhances the nucleation rate by a factor of around 10^7 for case 1 and 10^6 for case 2. THN theory can predict very high nucleation rate (even when $[H_2SO_4]$ is very low) as long as $[NH_3]$ is high enough. On the contrast, J^{IMN} is limited by ionization rate and the effect of ionization rate on J^{IMN} depends on $[H_2SO_4]$. The relative sensitivity of J^{IMN} to Q is much smaller than that of J^{THN} to $[NH_3]$. A detailed discussion about the effect of Q on J^{IMN} under different atmospheric conditions can be found in *Yu* [2002].

[18] By assuming the functional power dependence of nucleation rate on $[H_2SO_4]$ in the form of $J = const \times [H_2SO_4]^\alpha = const \times X^\alpha$, we can compare the sensitivity of J to $[H_2SO_4]$ from the values of α. For the portion of curves shown in Figure 2, the value of α is 6.9 for J^{THN} and 14.0 for J^{BHN} in case 1 and is 6.0 for J^{THN} and 15.7 for J^{THN} in case 2. Based on THN theory, the presence of NH_3 not only significantly increases the nucleation rates but also reduces the sensitivity of nucleation rates to $[H_2SO_4]$ (i.e, the values of α). Nevertheless, J^{THN} is still very sensitive to $[H_2SO_4]$ ($\alpha \geq 6$ for the conditions shown in Figure 1) which is unlikely to explain the observed $[H_2SO_4]^2$ dependence of J^{obs} on $[H_2SO_4]$ (i.e, $\alpha = 2$) [*Weber et al.*, 1996].

[19] The values of α for $J_{D_{crit}}^{IMN}$ at three different values of $[H_2SO_4]$ are also shown in Figure 2. Under the considered conditions, J^{IMN} is negligible when $[H_2SO_4] < \sim 3 \times 10^6/$ cm^3. J^{IMN} increase rapidly with $[H_2SO_4]$ when $[H_2SO_4]$ is relatively low ($\alpha > 14$ at $[H_2SO_4]$ of $< \sim 3 \times 10^6/$cm^3) but such increase slows down when $[H_2SO_4]$ becomes higher ($\alpha = 2$ at $[H_2SO_4]$ of $\sim 9 \times 10^6/$cm^3 and ($\alpha < 0.4$ at $[H_2SO_4]$ of $> \sim 4.5 \times 10^7/$cm^3). The main physics behind such a behavior is that at low $[H_2SO_4]$ the nucleation is limited by $[H_2SO_4]$ while at high $[H_2SO_4]$, nucleation is limited by ion concentration (or ionization rate). The dramatic change of α values for J^{IMN} in the range of $[H_2SO_4]$, where most of nucleation events in the atmosphere have been observed, is quite different from that predicted based on BHN and THN theories. The α value of ~ 2 when $[H_2SO_4]$ is slightly smaller than $1 \times 10^7/$cm^3 may somehow explain the $[H_2SO_4]^2$ dependence of J^{obs} on $[H_2SO_4]$ [*Weber et al.*, 1996]. However, we should be cautious about such comparison because $[H_2SO_4]$ changes rapidly during the observed nucleation events while we keep $[H_2SO_4]$ constant in our simulations. Some features of J^{obs}, for example the relatively high values of J^{obs} at very low $[H_2SO_4]$ may be explained by time delays inherent in the chemical-microphysical system under investigation [*Turco et al.*, 1998].

4. Summary

[20] We first investigate the time-needed (t_0) to establish a pseudo-steady state production rate of certain size particles when $[H_2SO_4]$ suddenly increases to a certain level. We find that t_0 is almost inversely proportional to $[H_2SO_4]$. In the two marine atmospheric conditions considered in this paper, to establish a pseudo-steady state production rate of particles with the size of critical embryo, it takes ~ 5 minutes and ~ 60 minutes at $[H_2SO_4]$ of $5 \times 10^7/$cm^3 and $5 \times 10^6/$cm^3, respectively. Note that at a given $[H_2SO_4]$, t_0 is shorter at a lower temperature as D_{crit}

is smaller. However, in the lower atmosphere where temperature is relatively lower, the average concentration of H_2SO_4 is generally lower which will increase t_0. For relative low values of $[H_2SO_4]$ and when $[H_2SO_4]$ changes rapidly, t_0 may be much bigger than the time period that $[H_2SO_4]$ can be treated as constant. In such cases, the assumption that pseudo-steady state distribution of critical clusters is achieved immediately following the changes in $[H_2SO_4]$, on which the classical nucleation theories are based, is no longer valid.

[21] The sensitivity of nucleation rates predicted by IMN theory (J^{IMN}) to $[H_2SO_4]$ has been investigated and compared to that of nucleation rates predicted by BHN and THN theories. Under the conditions considered in this study, J^{IMN} is very sensitive to $[H_2SO_4]$ when $[H_2SO_4]$ is relatively low ($< \sim 7 \times 10^6/$cm^3) but such sensitivity reduces as $[H_2SO_4]$ increases. If we assume that nucleation rate is proportional to $[H_2SO_4]^\alpha$, the value of α for J^{IMN} is >14, 2, <0.4 at $[H_2SO_4]$ of 3×10^6, 9×10^6, $4.5 \times 10^7/$cm^3, respectively. The dramatic change of α values for J^{IMN} in the range of $[H_2SO_4]$ where most of nucleation events in the atmosphere have been observed is quite different from that predicted based on BHN ($\alpha > 14$) and THN ($\alpha = \sim 6-7$) theories.

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