Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO$_2$ + OH reaction

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[1] We have measured H$_2$SO$_4$-H$_2$O nucleation rates ($J$) at atmospheric pressure, 288 K and 10–55 % relative humidity (RH). H$_2$SO$_4$ was produced from the SO$_2$ + OH → HSO$_3$ reaction and was measured with a chemical ionization mass spectrometer (CIMS). The CIMS-measured [H$_2$SO$_4$] that is required to produce the unit nucleation rate ($J$) at the residual [H$_2$SO$_4$] ranged from 10$^7$–10$^8$ cm$^{-3}$, but if wall loss is taken into account the threshold [H$_2$SO$_4$] was at the 10$^8$–10$^9$ cm$^{-3}$ range, much higher than the atmospheric conditions. The measured $J$ was proportional to [H$_2$SO$_4$] with the second power, much higher than the atmospheric conditions. The measured $J$ was proportional to [H$_2$SO$_4$] with the second power, but the RH effects were more pronounced at higher [H$_2$SO$_4$], indicating that RH is more important for aerosol growth in the H$_2$SO$_4$ rich environment. **Citation:** Benson, D. R., L.-H. Young, F. R. Kameel, and S.-H. Lee (2008), Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from the SO$_2$ + OH reaction, Geophys. Res. Lett., 35, L11801, doi:10.1029/2008GL033387.

1. Introduction

[2] Atmospheric observations show that nucleation takes place in a wide range of atmospheric conditions, much lower than the atmospheric conditions. The measured [H$_2$SO$_4$] that is required to produce the unit nucleation rate ($J$) at the typical sulfuric acid concentrations of ([H$_2$SO$_4$]) of 10$^6$–10$^7$ cm$^{-3}$ [Kulmala et al., 2004, and references therein]. Aerosol nucleation has been studied intensively by modeling simulations [Vehkamäki et al., 2002; Lucas and Akimoto, 2006], but these calculations contain high uncertainties, because they are not fully tested by experiments. The H$_2$SO$_4$-H$_2$O binary homogeneous nucleation (BHN) system is the most important atmospheric nucleation system, but there are only a limited number of experimental studies on this system [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006], because of the technical difficulties associated with laboratory nucleation studies including difficulties of measuring low [H$_2$SO$_4$] at atmospherically relevant conditions and wall loss of H$_2$SO$_4$. These previous H$_2$SO$_4$-H$_2$O nucleation studies were made at [H$_2$SO$_4$] from 10$^6$–10$^9$ cm$^{-3}$, RH from 1–60% and room temperature, and showed nucleation rates ($J$) ranging from 10$^{-3}$–10$^5$ cm$^{-3}$ s$^{-1}$ [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]. Most of these studies have also used vaporized H$_2$SO$_4$ gases from H$_2$SO$_4$ liquid samples at the residual [H$_2$SO$_4$] ≥ 10$^8$ cm$^{-3}$ [Wyslouzil et al., 1991; Ball et al., 1999; Zhang et al., 2004], and these studies could not reproduce the atmospherically observed $J$ under atmospherically relevant conditions. Berndt et al. [2005, 2006] used the SO$_2$ + OH → HSO$_3$ reaction (R1) to produce H$_2$SO$_4$ and for the first time, produced a unit nucleation rate (1 cm$^{-3}$ s$^{-1}$) at atmospherically relevant conditions (e.g., 6 × 10$^9$ cm$^{-3}$). However, Berndt et al. [2005, 2006] did not directly measure [H$_2$SO$_4$]; instead it was calculated from OH titration reactions by introducing various hydrocarbon compounds in a system that also contains high concentrations of ozone, water vapor, and OH, and UV light (in such a condition, highly oxidized low volatility organic compounds can also be produced).

[3] Wall loss of H$_2$SO$_4$ is one of the major challenges in nucleation experiments. Most previous studies [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006] have provided the residual [H$_2$SO$_4$] measured or estimated at the end of the nucleation reactor, whereas some have also calculated the initial [H$_2$SO$_4$] based on their conditions [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999]. Viisanen et al. [1997] and Ball et al. [1999] have characterized the wall loss. Laboratory studies of H$_2$SO$_4$-H$_2$O BHN have often investigated how $J$ depends on [H$_2$SO$_4$] and RH [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999], since such information can be directly used for testing theoretical models. While nucleation rate dependence on [H$_2$SO$_4$] has been investigated previously [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2006], the $J$ dependence on RH is not well established [Wyslouzil et al., 1991; Ball et al., 1999]. Also, it is important to understand how these newly formed particles grow to become cloud condensation nuclei, but aerosol growth rates have not been measured in laboratory studies.

[4] Here, we present laboratory studies of the binary H$_2$SO$_4$-H$_2$O system at the residual [H$_2$SO$_4$] (measured by CIMS at the end of the nucleation reactor) ranging from 4×10$^8$–3×10$^9$ cm$^{-3}$ and RH from 10–55 %. H$_2$SO$_4$ vapor was produced in-situ by gas phase reactions of SO$_2$, OH, O$_3$ and H$_2$O based on the above (R1), as occurring in the atmosphere and similarly to Berndt et al. [2005, 2006]. Wall loss factors (WLFs) of H$_2$SO$_4$ were calculated by assuming that wall loss is diffusion limited (auxiliary material). We report the laboratory-measured aerosol sizes, growth rates, $J$, and threshold [H$_2$SO$_4$] (corrected by WLF),
and compare them with previous laboratory studies and atmospheric measurements.

2. Experimental Setup

Our \( \text{H}_2\text{SO}_4\)-\( \text{H}_2\text{O} \) BHN kinetics experimental setup consists of four main components: (i) an OH generator with water vapor UV absorption, (ii) a fast flow reactor in which nucleation occurs, (iii) a CIMS which measures concentrations of the equilibrium \( \text{H}_2\text{SO}_4 \) vapor, and (iv) a TSI scanning mobility particle sizer (SMPS) (TSI 3936N76) (Figure S1). The water photolysis region is made of a PuriSil quartz tube where \( \text{OH} \) radicals form from water UV absorption (wavelengths <185 nm) with a mercury lamp (Pen-Ray Model 11SC-1) housed in a temperature-controlled box. The photon flux emitted from the lamp is stabilized with a constant \( \text{N}_2 \) flow and is measured with a CsI phototube (Hamamatsu Model R5764), which is calibrated against a NIST-certified Si photodiode (40599S). When \( [\text{SO}_2] \gg [\text{OH}] \), all \( \text{OH} \) radicals are rapidly converted to \( \text{H}_2\text{SO}_4 \) and the produced \( [\text{H}_2\text{SO}_4] \) are the same as \([\text{OH}]\).

The actual nucleation region (\( L = 82 \text{ cm}, \text{ID} = 5.08 \text{ cm} \)) is encompassed in a jacketed region through which a circulating bath is run to maintain a constant temperature. Only high purity standard gases (oxygen and \( \text{SO}_2 \)) (Linde Gas and Airgas Inc.), nitrogen gases blown off a liquid nitrogen tank, and the water vapor evaporated from deionized water are introduced in the nucleation region to reduce possible ammonia impurities. Ammonia contamination from liquid nitrogen gases is minimal (\(<20 \text{ pptv}\)) [Nowak et al., 2007]. We have used the silicon phosphates ammonia scrubber (Perma Pure Inc.) to test the effects of possible ammonia impurities in our system on the \( \text{H}_2\text{SO}_4\)-\( \text{H}_2\text{O} \) BHN experiments, and those effects were found negligible. The nucleation reactor’s pressure is also kept slightly higher than the air pressure to prevent a leak of the indoor air into the nucleation system.

The SMPS is composed of an ultrafine water-based condensation particle counter (CPC) (TSI Model 3786) and a nano-particle differential mobility analyzer (DMA) (TSI Model 308500) and measures aerosol sizes and concentrations in the diameter range from 2.5 to 102 nm, a size range much higher than the crucial clusters (\(~1 \text{ nm}\)). We assume that nucleation takes place in the entire region of the flow tube. The measured particle sizes and number concentrations increased with increasing nucleation time and these results confirm that this assumption is correct. Our results are however different from Ball et al. [1999] where nucleation takes place only in a portion of their nucleation reactor and this difference is probably related to the different methods used to produce \( \text{H}_2\text{SO}_4 \) vapor in these two studies.

The CIMS uses the \( \text{NO}_3 \) + \( \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4 + \text{HNO}_3 \) ion molecule reaction scheme to detect \( \text{H}_2\text{SO}_4 \) based on Eisele and Tanner [1993]. The detection limit of our CIMS is as low as \( 1 \times 10^3 \text{ cm}^3 \) at the atmospheric pressure. \( \text{H}_2\text{SO}_4 \) was measured at the end of the nucleation reactor and hence is the equilibrium or residual concentration rather than the initial aerosol precursor concentration. Wall loss factors (WLFs) of \( \text{H}_2\text{SO}_4 \) are estimated by assuming that wall loss of \( \text{H}_2\text{SO}_4 \) is diffusion-limited based on Hanson and Eisele [2000] (auxiliary material). Table 1 shows the detailed experimental conditions used in this study and the calculated WLFs. Figure S2 shows the evolution of the aerosol precursors in the nucleation reactor as a function of time.

3. Experimental Results

Figure 1a shows the measured \( J \) as a function of \( [\text{H}_2\text{SO}_4] \) at different RH and nucleation times. Overall, \( J \) varied from \( 10^{-3} \text{ to } 10^{-4} \text{ cm}^3\text{s}^{-1} \), at nucleation times from 20–66 s, RH from 11–38% and with residual \( [\text{H}_2\text{SO}_4] \) (measured by CIMS) from \( 4 \times 10^6 \text{ to } 3 \times 10^5 \text{ cm}^3 \). The CIMS-measured \( [\text{H}_2\text{SO}_4] \) that is needed to produce the unit \( J \) ranged from \( 10^3 \text{ to } 10^5 \text{ cm}^3 \), and when wall loss is taken into account, the threshold \( [\text{H}_2\text{SO}_4] \) ranged from \( 10^5 \text{ to } 10^3 \text{ cm}^3 \). The numbers of \( \text{H}_2\text{SO}_4 \) molecules in the critical clusters, \( n_{\text{H}_2\text{SO}_4} \), were derived from the slopes of curves for \( J \) vs \( [\text{H}_2\text{SO}_4] \) based on Kaschchiev [1982]. The derived \( n_{\text{H}_2\text{SO}_4} \) ranged from 2–10 with larger values as RH decreases, a trend consistent with other studies [Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]. At the

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Table 1. Experimental Conditions Used in the Present Study and the Wall Loss Factors Calculated by Assuming That Wall Loss is Diffusion-Limited

<table>
<thead>
<tr>
<th>Data Used</th>
<th>Particle Measurement Mode</th>
<th>NT(s)</th>
<th>RH, %</th>
<th>Initial ([\text{SO}_2]_0), (10^{15} \text{ cm}^{-3})</th>
<th>(\text{H}_2\text{SO}_4) Calculated From (\text{WLFb}, 10^5 \text{ cm}^3)</th>
<th>CIMS-Measured ([\text{H}_2\text{SO}_4]_b, 10^7 \text{ cm}^3)</th>
<th>([\text{H}_2\text{SO}_4]_b)-Particle, (10^3 \text{ cm}^3)</th>
<th>(J^r \text{ cm}^{-3} \text{s}^{-1})</th>
<th>(\text{WLF}^{\text{calc}})</th>
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<tr>
<td>Figure 1a</td>
<td>CPC</td>
<td>20</td>
<td>11–14</td>
<td>4.8–12</td>
<td>12.9–32.4</td>
<td>4.6–12.5</td>
<td>0.025–0.41</td>
<td>0.33–0.54</td>
<td>2.6–2.8</td>
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<tr>
<td>Figure 1a</td>
<td>CPC</td>
<td>54</td>
<td>16–13</td>
<td>3.86</td>
<td>0.32</td>
<td>3.1</td>
<td>15.31</td>
<td>11.9</td>
<td></td>
</tr>
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<td>Figures 1a and 2</td>
<td>SMPS/CPC^c</td>
<td>32</td>
<td>28–30</td>
<td>4.5–23</td>
<td>22.6–38.7</td>
<td>3.9–4.8</td>
<td>94.6–1800</td>
<td>130–5000</td>
<td>95.5–5.7</td>
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<tr>
<td>Figures 1a and 2</td>
<td>SMPS/CPC^c</td>
<td>60</td>
<td>26–38</td>
<td>12–40</td>
<td>1.6–54.1</td>
<td>0.058–0.078</td>
<td>5.6–80.4^d</td>
<td>38–4500</td>
<td>18.4–19.8</td>
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<td>Figure 1b</td>
<td>CPC</td>
<td>77</td>
<td>25–55</td>
<td>0.07–84</td>
<td>6.0–21.6</td>
<td>0.2–0.7</td>
<td>1.2–46.20</td>
<td>2.2–81</td>
<td>29.9</td>
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<td>SMPS/CPC^c</td>
<td>33</td>
<td>28–57</td>
<td>1.7–6.7</td>
<td>33.9–54.8</td>
<td>7.6–11.0</td>
<td>450–30800</td>
<td>970–3940</td>
<td>4.3–4.4</td>
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<td>2.5–10</td>
<td>46.0–360</td>
<td>0.4–0.6</td>
<td>4500–38600</td>
<td>4700–19000</td>
<td>9.1–9.3</td>
</tr>
</tbody>
</table>

^aAll experiments were made at the absolute temperature of 288 K, total flow of \( 1.3 \text{ to } 5.0 \text{ l min}^{-1} \), and at atmospheric pressure. The initial \([\text{H}_2\text{SO}_4]_0\) were estimated from the Wall Loss Factors (WLFs), the CIMS-measured \([\text{H}_2\text{SO}_4]_b\) and the measured \([\text{H}_2\text{SO}_4]_b\) in the particle phase (Figure S2), as shown in auxiliary material. Figure S2 also shows the time variation of aerosol precursors in the nucleation reactor.

^bFor these parameters, the ranges are the median value ranges.

^cNote, some data were taken by CPC alone and some by SMPS; the measured particle number concentrations were up to a factor of > 10 higher with the CPC mode than with the SMPS mode under the same experimental conditions.

^dIn these cases, \([\text{H}_2\text{SO}_4]_b\) in the particle phases were larger than those measured by CIMS and therefore, when estimating the initial \([\text{H}_2\text{SO}_4]_b\), \([\text{H}_2\text{SO}_4]_b\) in the particle phase become important.
Figure 1
CIMS-measured [H$_2$SO$_4$] from 1 $\times$ 10$^7$ – 1 $\times$ 10$^8$ cm$^{-3}$ (the corresponding [H$_2$SO$_4$] in the nucleation reactor from 3 $\times$ 10$^8$ – 5 $\times$ 10$^9$ cm$^{-3}$ with wall loss taken into account) (Table 1), RH of 22–55% and a nucleation time of 77 s, the number of water molecules in the critical clusters ($n_{H_2O}$) ranged from 11–15 (Figure 1b). These $n_{H_2O}$ values also decreased with increasing [H$_2$SO$_4$], consistent with the predictions from the homogeneous nucleation theories.

Figure 1. (a) The measured nucleation rates $J$ as a function of [H$_2$SO$_4$]. The [H$_2$SO$_4$] shown here with symbols are those measured by CIMS; horizontal bars show the calculated WLF values for each experimental condition. NT indicates the nucleation time. The solid lines represent linear fitting for log $J$ versus log H$_2$SO$_4$ curves. Also included are experimental results from Ball et al. [1999] (black dashed) and Zhang et al. [2004] (black dot) for similar temperature and RH conditions. For both these cited data, CIMS-measured [H$_2$SO$_4$] are shown without wall loss corrections; WLF of 22 was provided by Ball et al. [1999], and no WLF was provided by Zhang et al. [2004]. Not shown here are the Berndt et al. [2005, 2006] data because the [H$_2$SO$_4$] is much lower (10$^6$ – 10$^7$ cm$^{-3}$); but their value for $n_{H_2SO_4}$ is also 5. (b) The measured $J$ as a function of RH. The [H$_2$SO$_4$] shown here are the CIMS-measured [H$_2$SO$_4$]; for a nucleation time (NT) of 77 s, WLF is 29.9 (Table 1). The initial [SO$_2$] are also shown here. The lines represent linear fitting for log $J$ versus log RH curves. The measured nucleation rates depend on nucleation times because at longer nucleation times, wall loss and condensation loss of H$_2$SO$_4$ (Figures S2 and S3) become more important. A very similar feature was also seen by Wyslouzil et al. [1991]. The experimental conditions and WLFs for these data sets used in this figure are shown in Table 1 (the same for other figures).
The $n_{H_2O}$ values calculated from this study are higher than Ball et al. [1999] ($n_{H_2O} = 4–6$) and Wyslouzil et al. [1991] ($n_{H_2O} = 9$), likely because of lower [H$_2$SO$_4$] used in this study.

The measured aerosol sizes ($D_p$) were between 3–10 nm at the CIMS-measured [H$_2$SO$_4$] from 2 × 10$^6$ to 5 × 10$^8$ cm$^{-3}$ (corresponding to [H$_2$SO$_4$] in the nucleation region from 1.3 × 10$^6$–1.3 × 10$^{10}$ cm$^{-3}$ with a WLF of 8), RH from 22–30% and a nucleation time of 38 seconds (Figure 2). The $D_p$ increased with increasing [H$_2$SO$_4$], RH and nucleation time. At larger aerosol number concentrations and at larger $D_p$, condensation loss of H$_2$SO$_4$ became noticeable. For example, the CIMS-measured [H$_2$SO$_4$] were lower for largest aerosol sizes than those for smaller sizes (Figures 2 and S3). We also found that the measured $D_p$ was linearly proportional to log RH, showing a weak RH dependence of aerosol growth (Figure 3). However the slopes of $D_p$ vs log RH curves were steeper at higher [H$_2$SO$_4$], indicating that the RH effects on the aerosol growth are more pronounced at higher [H$_2$SO$_4$] conditions.

4. Discussions and Atmospheric Implications

An evident trend found from the present study is that $n_{H_2SO_4}$ decreases with increasing RH and $n_{H_2O}$ decreases with increasing [H$_2$SO$_4$] (Figure 1), consistent with classical nucleation theories [Seinfeld and Pandis, 1997] and with the trend found in previous laboratory works [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2006]. One objective of this kind of kinetic study is to provide experimental data to compare with nucleation predictions to test the theories. Recently, Yu [2007] provided the improved quasi-unity nucleation modeling calculations of binary H$_2$SO$_4$-H$_2$O nucleation. The model predicted $n_{H_2SO_4}$ ranged from 5–12 at [H$_2$SO$_4$] of 1 × 10$^{11}$ cm$^{-3}$, 30 % RH, and 298 K [Yu, 2007], consistent with those found in the present and other laboratory studies [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2006] which showed $n_{H2SO4}$ values of 2–10 overall.

The measured $D_p$ was linearly proportional to log RH (Figure 3), showing a weak RH dependence. However, those RH effects were more pronounced at higher [H$_2$SO$_4$], indicating that RH is more important for aerosol growth in a polluted atmosphere, an important atmospheric implication.

The measured aerosol growth rates are dependent on the above factors in a similar fashion and our results confirmed this trend. The growth rates estimated in our study from the aerosol growth from different nucleation times are roughly from 160–490 nm hr$^{-1}$. The growth rates increased with increasing [H$_2$SO$_4$], consistent with atmospheric observations [Kulmala et al., 2004] which showed a positive correlation between the growth rate and non-volatile vapor concentration. Our growth rates are however much higher than those found in the atmosphere (usually between 1–20 nm hr$^{-1}$) [Kulmala et al., 2004]; this is because of the higher [H$_2$SO$_4$] range used in this study than the atmospheric conditions.

There has been a debate on the threshold [H$_2$SO$_4$] required to produce the unit J. Atmospheric observations often show that unit nucleation rates can be achieved even at
[H$_2$SO$_4$] of 10$^6$ cm$^{-3}$ [Weber et al., 1999; Birmili et al., 2000], whereas BHN theories cannot reproduce the unit $J$ at this low [H$_2$SO$_4$] [Kulmala et al., 1998; Vehkamäki et al., 2002]. Our study shows that the threshold [H$_2$SO$_4$] is on the order of 10$^5$–10$^7$ cm$^{-3}$ (with wall loss taken into account) (Figure 1a). This threshold is lower than those found in the liquid H$_2$SO$_4$ sample experiments [Ball et al., 1999; Zhang et al., 2004] (Figure 1a), but is still higher than those by Berndt et al. [2005, 2006] which also used R1 to produce H$_2$SO$_4$ and higher than the atmospheric conditions. Furthermore, the laboratory-produced $J$ are usually proportional to [H$_2$SO$_4$] with the second to thirtieth powers [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2005, 2006] (this study), whereas the atmospherically-observed $J$ are often linearly proportional to [H$_2$SO$_4$] [e.g., McMurry and Eisele, 2005]. These higher threshold of [H$_2$SO$_4$] and the larger number of H$_2$SO$_4$ in the critical clusters observed in the laboratory BHN studies compared to those measured in the atmosphere suggest that ternary species other than sulfuric acid and water can be important for atmospheric aerosol nucleation and growth.

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References


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