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Atmospheric
Chemistry
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Discussions

Interactive comment on “Laboratory studies ofH_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results” *by* L.-H. Young et al.

L.-H. Young et al.

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Response to Reviewer III

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We thank the reviewer for helpful comments and revised our manuscript accordingly. The summary of our major revisions are described in our summary response file, separately. Please also see the revised manuscript for detail. Below, we provide detailed point-to-point response to the review.

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Anonymous Referee #3

The topic is very interesting and important one, and the MS can be published in ACP after major improvements.

1) In introduction the recent findings of atmospheric nucleation should be mentioned

(e.g. Kulmala et al., 2007a). Particularly the finding of the size of recently formed clusters in atmospheric conditions should be compared with present laboratory findings.

RE: We agree. Introduction, the first paragraph: “The current nucleation theories are not fully tested and constrained by laboratory observations. Recently, Kulmala et al. (2007a) showed direct evidence of aerosol nucleation by measuring neutral clusters and small aerosol particles at the 1.5 nm size range in the boreal atmosphere and suggested that their findings support the cluster activation theory of atmospheric aerosol nucleation proposed by Kulmala et al. (2006).” Section 5.2, the 2^{nd} paragraph: “Recently, Kulmala et al. (2006) proposed an activation theory of neutral clusters containing one or two H_2SO_4 molecules to explain the field observations. While recent field studies of small neutral clusters (Kulmala et al., 2007a) also support this theory, but further experimental work will be required to prove this new theory.”

2) The closure between sulphuric acid source and sink with corresponding concentration should be investigated. During this investigation also the initial sulphuric acid concentrations should be shown, not only the final (residual) ones. The assumption that $[H_2SO_4]$ = [OH] should be verified.

RE: This is an important comment. We did test experiments to see how the [OH] are related to the residual [H2SO4] measured at the end of the nucleation reactor and WLFs (Table 2 and Figure 6). In conclusion, the [OH] produced from water vapor photolysis are on the same order as the initial [H2SO4] calculated from the CIMS-measured residual [H2SO4] and wall loss of H2SO4, within experimental uncertainties (Table 2 and Figure 6). First, The CIMS-[H2SO4] determination is based on Huey (2007) (Section 2.4) from the measured $NO3^-$ and $HSO4^-$ ion signals and the reaction time in the ion-molecule reaction region of the CIMS. Field studies have proven that this method is valid (Huey 2007; Eisele and Tanner, 1993) (Section 2.4). Our experimental results also show the CIMS measurements also have a high stability over an 8 hour measurement period (relative standard deviation of < 10 % (Figure 3a). We have calculated the initial [H2SO4] from the residual [H2SO4] measured by CIMS and wall loss factors (WLFs) (Section 3.2). Table 2 shows these initial [H2SO4], along with the CIMS-measured residual [H2SO4] and WLFs. Table 2 also includes the initial [OH] produced from water vapor photolysis experiments. Since for all experimental conditions [SO2] $>>$ [OH], one can expect that the produced [OH] are the same as the initial [H2SO4], when CO impurities are negligible (our CO scrubber tests show that [CO] is only at the 200 ppbv level). As shown in Table 2, the produced [OH] are indeed on the same order as the initial [H2SO4] within experimental conditions, estimated from WLFs and the CIMS-measured residual [H2SO4]. Figure 6 also shows how gas phase species evolve as a function of time in the nucleation reactor for the typical experimental conditions and gives an example of [OH] = initial [H2SO4]. OH dilution with SO2, O2, and N2 in the mixer is not important under our experimental conditions, as the main flow is N2 used to bubble water (Section 2.2). In addition, the OH and SO2 reaction time is very short under our experimental conditions (e.g., 1 ms) (Figure 6). So it is reasonable to assume that the majority of [OH] is converted to [H2SO4] and our results show this is the case (Table 2 and Figure 6). We have also verified our WLFs calculations with the simultaneous measurements of [H2SO4] at the beginning and at the end of the nucleation reactor with two CIMSs and found that WLFs, calculated by assuming H2SO4 wall loss is diffusion limited, are consistent with observations (Section 3.1; Figure 5). For the detail, please see the mentioned sections in the revised manuscript.

3) What is the status of Benson et al. MS?

RE: Benson, D. R. et al., Laboratory-Measured Sulfuric Acid and Water Homogeneous Nucleation Rates from the SO2 + OH Reaction, *Geophys. Res. Lett.*, 35, L11801,

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Doi:2008GL033387.

4) CPC detection efficiency is a key point to consider. There is a clear need to make a proper calibration and to show the results of the calibration. Water CPC and butanol CPC might give different values (see Kulmala et al., 2007b), and therefore proper calibrations are needed. Also the obtained data should be shown.

RE: We agree. Section 2.3 the 4^{th} paragraph: “Nucleation rates shown in the present study were measured only with water-CPC (TSI 3786). But we also made comparisons with water CPC and butanol-CPC (TSI 3776) and there was an almost linear relation between these two measurements when sampling the particles generated in the nucleation reactor, with the water-CPC concentrations about 8 times higher than the butanol-CPC concentrations. On the other hand, when sampling the laboratory room air, the concentrations measured from WCPC were only $\sim$ 7% higher than those measured by the butanol-CPC. Since the particles generated in the nucleation reactor are presumably pure H_2SO_4 particles whereas the particles in the lab air are more mixed with H_2SO_4(or sulfate) and organic components, these results indicate that water can activate, and condense on, H_2SO_4 particles more effectively than butanol, consistent with Kulmala et al. (2007b).”

5) Although there are a lot of results, they are not shown in the proper way. All results should be given in tables. All results should also be given as a function of initial and residual [H_2SO_4] not only residual. It is also important to plot results in X-Y plots.

RE: We agree. Figures are revised as a function of [H2SO4] (as opposed to as a function of time previously). Also for [H2SO4], we have also included WLFs in these revised figures so that we can estimate the initial [H2SO4] from the residual [H2SO4] and WLFs. We have revised Table 2 to show the detailed experimental conditions of [OH], initial [H2SO4], residual [H2SO4] and WLFs.

6) Since the same residual [H2SO4] gives different nucleation rates there are some-

thing unclear in the experiments. In my point of view the time for one experiment is probably too short. In several nucleation experiments (like in Viisanen et al., 1997) the time is much longer. Other possibility is that the detection efficiency of used CPCs and SMPS is not good enough to detect all nucleated particles.

RE: This stability issue is an important comment and we have performed stability tests of H2SO4 and particles (Figure 3 and Section 2.3). H2SO4 measurements show very high stability with relative standard deviation of $<$ 10 % (Figure 3a). On the contrary, we found some stability issue with particle measurements (Figure 3a). The particle concentrations often rise in the beginning taking a few minutes then decline slowly with time to become stabilized. These stabilization times are often quite long (e.g., 3 hours). But the initial concentrations are usually about a factor of 5 higher than those under steady state conditions after 3 hours (Figure 3b). We have taken into account this difference for particle measurements and nucleation rate calculations. As for wall loss of [H2SO4], as shown in Section 3.1, wall loss is diffusion limited and wall loss is a first order rate process (Figure 4 and Section 3.1). Figure 6 shows in detail how this process takes place as a function of time in the nucleation reactor." Also, Section 2.3, the 3^{rd} paragraph: "When the CPC is operated with the nano-SMPS, some of the particles smaller than 2.5 nm may be excluded in the nano-DMA, hence further contributing to the concentration difference."

7) It would be good to have some clear explanation why to use 4 and 19 s for nucleation time.

RE: These is no specific reason for us to have chosen these two specific residence times (in Benson et al., 2008, a greater variety of residence times are chosen). We rather chose two quite different values to examine wall loss factors and processes. "Since wall loss is simply a first order rate process, WLFs can be examined by using different residence times. (as shown in Section 3.1, the 1^{st} paragraph).

8) The argument that [H_2SO_4] cannot explain the observed growth seems not be valid.

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At least [H_2SO_4] can explain almost all the growth. However, proper calculations and comparison should be shown.

RE: We agree. We have included new calculations of growth rates calculated from three different methods based on the measured aerosol sizes, residence time, and the initial [H2SO4] and these results show that growth rates ranged from 100- 500 nm hour-1 (please see Section 5.3 for the detailed discussion).

9) On removal of O2: how it was determined? What was the concentration after removal?

RE: We have used high purity standard gases (especially for nitrogen gases which are the main flow, we used those vaporized from liquid nitrogen to minimize the impurities) but we did not make extra efforts to remove O2 from these standard gases and also did not attempt to detect O2 impurities, as O2 effects are not the focus of our study.

10) The main result figure (14) shows that at the nucleation rate [H_2SO_4] varies more than factor of 10. It might also indicate the varying contribution of ions. It is important

to comment that. The recent findings by Winkler et al. shows that ions are activating (nucleating) much more effectively than neutral clusters or homogeneous nucleation do occur (Winkler et al., 2008).

RE: We agree. Section 5.2, the last paragraph: “Recent findings by Winkler et al. (2008) showed that organic vapors can easily condense on small charged, preexisting seed aerosol particles starting from 1.2 nm and undergo heterogeneous nucleation at lower saturation ratios. Since we have not intentionally applied any ion sources in the nucleation reactor, there are minimal charged clusters or small particles that can act as seed particles for heterogeneous nucleation with the low production rates of ions by the natural sources at the ground level (Lovejoy et al., 2004). We also believe that there are minimum organic vapor in our system and therefore, heterogeneous nucleation on charged clusters are negligible. But this is an interesting area we want to look into in

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the future.”

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