Atmos. Chem. Phys. Discuss., 8, S4835–S4841, 2008
www.atmos-chem-phys-discuss.net/8/S4835/2008/

Atmospheric Chemistry and Physics 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.

Received and published: 15 July 2008

Response to Reviewer I

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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.

Anonymous Referee #1

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Interactive Discussion

Discussion Paper

General comments:

The manuscript is dealing with experimental findings from laboratory regarding new particle formation by oxidizing SO_2. This topic is very important for atmospheric science and at the moment it is still open what the most important nucleation process is. The authors present a couple of experimental results for different conditions, e.g. residence time, relative humidity, precursor concentrations. These data are worth to publish. But, while reading this manuscript few questions arose, mainly technical points.

Before publication a major revision is necessary.

Specific comments:

1. In text, figures and tables it is stated that residual H_2SO_4concentration at the end of the flow tube was in the range 10^8 - 10^{10} molecule cm^{-3}. At page 5 and figure 2b OH concentration in the photolysis zone is given with about 10^9 molecule cm^{-3}. Downstream the photolysis zone this gas stream is diluted with N_2/SO_2 before entering the nucleation reactor, see figure 1. That means that after dilution maximum OH is $< 10^9$ molecule cm^{-3} and after total conversion via OH + SO_2 maximum H_2SO_4 is $< 10^9$ molecule cm^{-3}. Given wall loss factors are in the range 2 to 12 resulting in maximum H_2SO_4 at the end of the tube $<$ (0.83 - 5) x 10^8 molecule cm^{-3} neglecting any contribution from condensation. The authors should clearly explain the discrepancy between maximum OH level and residual H_2SO_4 measured. Do they assume additional channels for H_2SO_4 generation other than OH + SO_2? What is the accuracy of H_2SO_4 determination?

RE: This is an important point and we would like to clarify. 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 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 3.1). 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 uncertainties, 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.

1. What is the photolysis time, page 5? What is the dilution factor for the OH/N_2 gas stream in the mixing region, figure 1?

RE: Photolysis time is between 0.08 – 0.43 s, depending on the nitrogen flow rates. As shown in Table 2, the dilution factor of OH/N2 is less than 18% by SO2 dilution and is nearly zero by O2 (Section 2.2).

1. The WLFs depicted in figures 3a and b are incorrect, log WLF is not about 10 or in the range 10^1 to 10^6 !

RE: Corrected.

1. H_2SO_4 was produced via R1 - R3. For chosen conditions, i.e. SO_2, O_2 and H_2O concentrations, the time scales should be given needed for complete conversion of OH, $HOSO_2$, and SO_3. What was the residence time in the mixing zone? E.g. the data for a 4 sec nucleation experiment given in figure 6b: Using k(OH+SO_2) = 1.5 x 10^{-12} for 0.03 ppm SO2 (7.4 x 10^{11} molecule cm^{-3}), for a 90% OH conversion 2.1 sec are needed and for a 99% OH conversion 4.2 sec!!!

RE: The entire residence time in the mixing region is typically 0.3 s where the mixing time corresponding to the SO2 + OH reaction is about 0.15 s for a typical total flow of 5 lpm, since the diameter of this mixing region is 2.24 cm and its total length is 6 cm but the distance between the SO2 introduction and the start of the nucleation reactor is 3 cm. It is correct that for 7.4 x 10^{11} molecule cm^{-3} SO2, the 99%-conversion time is 4.2 sec, as the reviewer pointed out. Similarly, for 7.4 x 10^{13} molecule cm^{-3} SO2, the 99% conversion time is 0.04 s, on the other hand. For most of experimental conditions, the SO2 used is $>$ 7.4 x 10^{12} molecule cm^{-3}, so the 99% conversion time is $<$ 0.4 s and the 90% conversion time is $<$ 0.2 s. Also, it is possible that the SO2 + OH reaction takes place continuously in the nucleation reactor (simultaneously with nucleation). But since the nucleation zone is about 40 cm (section 3.3), the SO2 + OH reaction is likely to complete well before nucleation completes.

What is the reason for the very low O_2 mixing ratio in N_2 of 0.001/(1.7 - 5.3)?

RE: We have realized that O2 is not a critical factor for R1-R3, and found that even such low concentrations of O2 can allow the reactions to run well (please also see below our response related to this).

1. Total residence time in the nucleation region was taken for the nucleation time for J-calculations. From my point of view, total residence time stands only for maximum nucleation time. For a wall loss factor of 2 (neglecting condensation) and a power equation, Eq.7, with n = 5 the ratio J(start)/J(end) = 1 / 0.03. And for a wall loss factor of 12 the ratio J(start)/J(end) is 1 / 0.000004. That shows that nucleation is inhomogeneous with time in this experiment. Ball et al. (1999) defined only a part of the tube as the "nucleation zone". The authors should discuss this topic and the consequences for J vs. H_2SO_4.

RE: We agree and have included simulation results of nucleation region now (Fig. 7 and Section 3.3). Briefly, we have conducted numerical simulations of aerosol nucleation as a function of axial position of the nucleation reactor based on the nucleation and condensation growth processes and from the measured aerosol size distributions and [H2SO4]. These calculations show that nucleation zone is with about 40 cm (a half of the nucleation tube length). This factor of 2 (residence time vs nucleation time) is also taken into account for nucleation rates.

1. Page 11: The authors did not observe clear effects regarding H_2SO_4 and produced particles switching off O_2 in the carrier gas. What does it mean "without O_2"? What is the residual O_2 concentration in the carrier gas under conditions "without O_2"? Is it enough for converting $HOSO_2$ via R2?

RE: As mentioned earlier, we have seen that [H2SO4] forms from very low O2. We did not attempt to detect the impurity O2 concentrations in standard gases, as this is not the focus of our study from the nucleation view point.

1. Page 12 and figure 5: It is confusing to see the particle number depending on the SO_2 concentration in the bottle. Was the purity of the 100 ppm SO_2 bottle checked?

RE: Section 4.1 last paragraph: “This difference occurs probably because of the incomplete mixing of SO_2 gases with other gas species in the fast flow reactor. Because SO_2 molecules were released near the centerline of the flow reactor, it would take a longer time for SO_2 molecules to be vigorously mixed with OH radicals at lower mixing ratios than at higher mixing ratios. The flow ratios of Q_{SO2} to Q_{total} were from 0.03 - 0.15 and from 0.025 - 0.04 for the 1 ppmv- and 100 ppmv-SO_2 cylinder experiments, respectively. Because its Q_{SO2} to Q_{total} ratios were larger than that for the 100-ppmv cylinder experiment, we can expect a better mixing with the 1-ppmv cylinder.” We did not check impurities of SO2 bottles, except that we performed CO and ammonia scrubber tests and these tests show that there are minimal CO and NH3 impurities in the system (Section 2.2)

1. In the figures in some cases there is an increase of particle number with time for constant H_2SO_4 visible. What is a possible explanation for this behavior? Are there saturation effects regarding the wall loss of H_2SO_4?

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. This 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.

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