

Interactive comment on “Photolytically-Generated Sulfuric Acid and Particle Formation: Dependence on Precursor Species” by David R. Hanson et al.

Anonymous Referee #2

Received and published: 28 February 2019

The paper by Hanson et al. reports on measurements made with a photolytic flow reactor (PhoFR). The PhoFR is used for nucleation studies where new particle formation is initiated from reactions involving mainly sulfuric acid and water. Additional measurements were made by adding base molecules, i.e., either diluted ammonia or dimethylamine are added to the flow reactor. The sulfuric acid is generated from the photolysis of HONO and further reactions involving SO₂, O₂ and H₂O. After a reaction time of approximately 30 s the particle size distribution is determined with a nano-differential mobility analyzer and a condensation particle counter using diethylene glycol. The measured size range covers diameters from approximately 2 nm to the largest sizes the particles can reach after the short reaction time, i.e., ~10 nm. The particle number from integration of the size distribution is used to derive new particle formation rates.

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With this information, the values from the present study are compared with other experiments and especially for the binary experiments (sulfuric acid and water); the data from the present study agree well with other data from the literature. For the ternary experiments involving ammonia, some discrepancy is reported. Further results are presented that show the variation of the integrated particle number and the particle size with the concentration for different gases. Results from a model involving various gas-phase reactions and the photolysis of HONO are shown for a comparison. Hanson et al. are also suggesting that a reaction between HO₂ and SO₂ could be relevant for forming sulfuric acid for the conditions of their flow tube experiment. I mainly agree with the conclusions drawn by the authors and the experimental data are mostly carefully evaluated and discussed. However, there is one major concern I am having regarding the experiments that involved ammonia (see below). After this point is addressed in a revised manuscript, I recommend publication in ACP.

(1) The bases (either ammonia or dimethylamine) are added from a sidearm into the flow reactor. The concern I am having is that this geometry does not ensure proper mixing and homogeneous distribution of the base. This possibility should be discussed and ideally, it should be evaluated in how far the mixing is homogeneous and if incomplete mixing could have influenced the results. For example, the results shown in Figure 7 suggest a relatively weak dependency of particle formation with the ammonia mixing ratio that is not consistent with other studies cited by the authors. Could this be related to the way the base is introduced into the flows? Another factor that can have an influence on the ammonia concentration is the mesh that is present in the flow reactor. It seems that the diluted NH₃ needs to pass that mesh before it can contribute to new particle formation. Almost certainly, some of the ammonia will be lost on the surfaces of the mesh, especially since its surface is acidic (as it has been soaked in a dilute sulfuric acid solution). More discussion related to these questions is required in the revised manuscript.

Further comments:

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P4, L4: Please use the correct spelling for some of the references (e.g., Sipilä et al. but also others). In addition, the references should be checked; for some of them, the year is not correct in the list or has not been cited correctly in the text

P3, L8: $\mu\text{mol} / \text{mol}$?

P3, L12: I think the word “additions” should be deleted

P4, L12: The year is missing here for the reference to Lovejoy et al.; this is the case also for other references in the main text

P5, L4: Does the outcome of the model depend on the flow setting? What mode is the “correct” one?

P5, L14: As can be seen from Fig. 1a the base is added from a sidearm at the end of the conical glass piece. Based on the geometry and the rather low flow rates it seems unlikely that the base is equally distributed over the whole cross section of the reactor. Has the possibility of inhomogeneous mixing been examined?

P5, L27: “. . . data were binned . . .”; please check the whole manuscript and use plural when using the word data

P6, L7: In the SI a detailed definition for the leading edge is provided; it would be good to provide a reference here to the SI regarding this exact definition

P7; L23: A definition for Z is missing

P8, L10 to L11: The process described here (scavenging of H_2SO_4 on the particles) is particle growth by condensation, which should be linear with the concentration of the condensing vapor (see, e.g., Nieminen, T., et al., 2010 ACP). Therefore, I do not understand this argument.

P9, L1: It would be good to include also curves from the model that do not include the $\text{HO}_2 + \text{SO}_2$ reaction in order to see the difference.

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P9, L6: ppmv instead of pptv?

P9, L12 to L16: I might have missed this but how exactly is the nucleation of particles modeled? The model needs to include evaporation rates for the smallest clusters. How are they obtained?

P9, L28 to L30: In this context, it should be noted that the factor of a 100 refers to the ratio of experiments with several hundred pptv and 4 pptv (which is the estimated contaminant level at 292 K in the Kürten et al. (2016, JGRA) study). For lower baseline (contaminant) NH₃ the enhancement factor is very likely much larger.

P9, L32: Is the conclusion then that the contaminant ammonia level is ~70 pptv for the set-up of the present study? This higher contaminant level (relative to the CLOUD experiment) could possibly explain the differences between the present and the Kirkby et al. (2011, Nature) study (Fig. 11).

P9, L33: Delete the word “base”

P10, L5: Replace “red squares” with “open squares”

P10, L10: The slope in Fig. 7 seems to be closer to 0.5 than to 1. How can this be explained?

P11, L24: Delete the word “and”

P13, L33-L34: This is one possibility; however, further discussion regarding the uncertainties of the present study is necessary. First, how would inhomogeneous mixing (of NH₃) influence the outcome of the present study? Second, is it possible that NH₃ is lost on the Teflon screen between the conical and the cylindrical glass pieces? It is mentioned that the screen was soaked in a dilute H₂SO₄ solution. Therefore, it could be that a significant fraction of NH₃ was lost on the mesh, which could lead to lower N_p in comparison to the previous studies (Glasoe et al., 2015 JGR and Hanson et al., 2017 JPhysChemA).

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P22, Fig4, L4: Please include “the CPC” before “raw count rate”

P23, L4: “orange line”, please check

SI:

P6, S5.2: The PTrMS is mentioned here. In terms of checking the homogeneity of NH₃ in the flow through the reactor, this instrument could possibly be used to measure ammonia at the outlet of the reactor when the lights are off.

P7, L3 to L4: References are missing here and the last sentence is incomplete.

P7, end of section S5.2: It should be explained why exactly this is consistent with expectations.

P7, S6, end of first paragraph: It is mentioned here that N_p increases with time for a set NH₃. If this is the case, how are the results with ammonia exactly obtained? Were the data only evaluated after a long enough waiting time? How long was this period and did the N_p level off eventually for all measurements?

P8, Table 1: The model does not seem to include the photolysis of NO₂. This can lead to an increased NO concentration and in turn increase OH (from HO₂ + NO). Photolysis of H₂O₂ can further enhance the OH level. When these reactions are implemented, is there still a need to include the HO₂ + SO₂ reaction? Furthermore, is the presence of HNO₃ further considered? It could possibly also be taken up by the aerosols.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1355>, 2019.

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