

Interactive comment on “SO₂ oxidation products other than H₂SO₄ as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications” by et al.

et al.

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We thank referee 1 for the useful comments.

This paper provides some interesting possibilities but does not support them very well. It is true that there are still discrepancies between field observations of nucleation and well defined mechanisms studied in the laboratory. While this does suggest that we are still missing something, there are many things that may help to stabilize small sulfuric clusters such as those containing two sulfuric molecules, and these possibilities have just begun to be explored.

Answer. True that the atmosphere is full of substances whose potential to nucleate with sulfuric acid has not been explored. However, our suggestion resolves contradictions also between different laboratory experiments conducted at clean conditions.

There is really no evidence for HSO₅ in the atmosphere or that it is a significant product of the OH/SO₂ reaction.

Answer. As referee 3 points out, this paper is "of course speculative";, and the results are "naturally not conclusive but they provide a basis for further discussions and investigations". True that there is no evidence for HSO₅ in the atmosphere or that it is a significant product of the OH/SO₂ reaction, but there is no evidence to the contrary, either; the best information from the lab leaves open an up to 10% pathway for HSO₅ formation in the OH/SO₂ reaction.

There is also mounting evidence that much nucleation occurs at relatively warm temperatures, and including data measured at Hyytiälä seems to depend on the square of the concentration of sulfuric acid (Kuang et al (2008), Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, J. Geophys. Res., 113, D10209, doi:10.1029/2007JD009253.) It is then unclear how HSO₅ would account for this squared dependence which is observed (HSO₅ clusters?). As suggested by this paper the HSO₅ dependence would be similar to the sulfuric acid dependence, but if HSO₅ radicals were to react with some organic compound to form a cluster that might grow into a new particle, the particle formation rate would only depend linearly on sulfuric acid concentration.

Answer. Kuang et al. find that nucleation rate depends on squared concentration of sulphuric acid concentration, however, e.g. Sihto et al. and Riipinen et al. find the dependence during individual nucleation events to vary from linear to squared. Our own multivariate analysis finds closer to linear dependence. So we do not think it is at all clear that the dependence should always be squared. Besides, our hypothesis only demands that the dependence is first or higher power. The HSO₅ dependence

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should be similar to the H_2SO_4 dependence, but the referee neglects our suggestion that H_2SO_4 nucleates heterogeneously on the HSO_5 reaction products. As long as only a fraction of the reaction products actually nucleate (see also our reply to referee 2), the observed dependence is also influenced by the number of H_2SO_4 molecules involved in the heterogeneous nucleation (see e.g. Vehkamäki et al.: Heterogeneous multicomponent nucleation theorems for the analysis of nanoclusters. J. Chem. Phys. 126, Article Number 174707, 2007). Thus, if one H_2SO_4 molecule is required for the heterogeneous nucleation, the apparent dependence on nucleation rate on sulphuric acid concentration is squared. On the other hand, if all reaction products of HSO_5 nucleate heterogeneously (or "activate") the dependence is linear. We will clarify all of this in the revised paper. We will also mention the caveat that in the experiments of Part 1, vaporized sulphuric acid seemingly had no effect on the nucleation or growth of particles produced by SO_2 oxidation. However, as discussed in revised Part 1, heterogeneous oxidation of SO_2 by H_2O_2 may have accelerated particle growth and masked the influence of vaporized H_2SO_4 on growth rates.

My largest concern is that there could have been large uncertainties in the sulfuric acid concentrations in the nucleation zone of the laboratory experiments particularly for the liquid sulfuric source. The sulfuric acid concentration was apparently only measured near one of the two sources of gas phase sulfuric acid and not in the nucleation zone. Losses of sulfuric after the long transport times of about one to several minutes in this experiment were probably much larger than calculated, particularly if any flow turbulence was encountered. This is, however, more true for one part of the experiment than the other where sulfuric acid was photochemically produced much further down the flow tube. Nucleation rates were measured to be much higher from the latter photochemically production region. These laboratory measurements were described in a companion paper that I think was previously submitted to GRL. I assume this paper was rejected by GRL since the latter laboratory paper or a paper very similar to it is now being submitted to ACP. Many of the conclusions of the present paper depend strongly on the laboratory paper so they should probably be published as one paper so

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that the reader can evaluate the experimental portion of this research.

Answer. We would like to point out that the results for vaporized sulphuric acid are well in accord with other results in the literature (we will add a figure showing this), so if there is a problem, then the other studies have problems, too. It can be stated once more that H₂SO₄ loss cannot be higher than the diffusion controlled limit. Assumption of diffusion limit is in line with measurements of Hanson and Eisele 2000, using similar experimental conditions. Occurrence of any turbulences or eddies (whatever the source should be? gas mixture is well mixed before entering the reaction zone, the whole equipment is well thermostated!) would result in significant fluctuations in the number concentrations and size distributions (due to their inherent instability) measured at the tube outlet. Such fluctuations were never observed during our experiments.

Other comments: On page 12 (section 3.1) in the paragraph starting "Stockwell and" it is suggested that HSO₅ might be a significant product of the SO₂/OH reaction. First there is no direct evidence for the presence of HSO₅.

Answer. True, but it should be noted that the possible reaction pathway producing HSO₅ has not been investigated (to our knowledge) since 1987, when it was indirectly shown that more than 90% of OH radicals are regenerated. Nowadays the experimental possibilities for narrowing down the remaining uncertainty are probably better.

Second, it is not at all clear that, if formed, HSO₅ could survive in the atmosphere long enough to interact with peroxy radicals or maybe large organics, which would probably also be in very low concentrations. It might well rearrange to give SO₃ and HO₂ or react with other more abundant O₂, H₂O, O₃ etc.

Answer. The decomposition step is possible producing SO₃ and HO₂ as well as a couple of bimolecular reactions. Probably, first HSO₅ undergoes reactions with H₂O and than the hydrated species react with other HO₂, SO₂, RO₂ etc., but all is speculative at the moment. Rough estimates regarding the HSO₅ atmospheric fate are given by Davis et al. GRL, 6, (1979), p.113.

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Third, if HSO₅ did react with a peroxy radical, why should we think that this would lead to a stable nucleating particle?

Answer. Quantum chemical calculations (M. Salonen et al, Atmos. Res., in press) indicate that the self reaction product of HSO₅ forms a rather stable complex with H₂SO₄. It is quite possible that other reaction products of HSO₅ would also. Besides, this would explain a number of discrepancies between different laboratory and atmospheric nucleation measurements.

On page 13 (section 3.1) in the paragraph starting "As an alternative"; it is suggested that sulfuric acid nucleation should not occur within a butanol based particle detector. This is not always the case, since butanol can react with sulfuric clusters in the detector. The authors should see: Hanson et al, Aerosol Science and Technology 36: 5548211;559 (2002).

Answer. Yes, butanol can react with sulfuric acid clusters. However, if the results of Berndt et al. are an artifact produced by sulphuric acid cluster reactions with butanol, then almost all of atmospheric nucleation data must be an artefact as well, because they have been measured at similar sulphuric acid concentrations, using a similar device. We do not find this very plausible. Furthermore, for sufficiently large particles, number concentrations from DMPS- SMPS- and integral counter measurements using butanol-based and H₂O-based counters are in good agreement! There are no indications for any counter-based nucleation!

Overall this paper seems like a way of explaining away experimental differences more than finding evidence for a new nucleation mechanism. Sulfuric acid and other trace compounds like ammonia need to be measured in, or at least at both ends of the nucleation zone, before this argument can be made credible.

Answer We are presenting a hypothesis that would solve many discrepancies found between different laboratory and atmospheric datasets. Together with the results presented in Part 1, we believe we have a strong case with a number of independent

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indirect evidence. We hope that we could convince others to start searching for direct evidence that could either prove or disprove our hypothesis.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9673, 2008.

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