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## ***Interactive comment on “SO<sub>2</sub> oxidation products other than H<sub>2</sub>SO<sub>4</sub> as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications” by et al.***

**Anonymous Referee #1**

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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. There is really no evidence for HSO<sub>5</sub> in the atmosphere or that it is a significant product of the OH/SO<sub>2</sub> reaction. There is also mounting evidence that much nucleation occurs at relatively warm temperatures, and

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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 HSO<sub>5</sub> would account for this squared dependence which is observed (HSO<sub>5</sub> clusters?). As suggested by this paper the HSO<sub>5</sub> dependence would be similar to the sulfuric acid dependence, but if HSO<sub>5</sub> 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. 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 that the reader can evaluate the experimental portion of this research. Other comments:

On page 12 (section 3.1) in the paragraph starting “Stockwell and”; it is suggested that HSO<sub>5</sub> might be a significant product of the SO<sub>2</sub>/OH reaction. First there is no direct evidence for the presence of HSO<sub>5</sub>. Second, it is not at all clear that, if formed, HSO<sub>5</sub> could survive in the atmosphere long enough to interact with peroxy radicals or maybe large organics, which would probably also be in very low

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concentrations. It might well rearrange to give  $\text{SO}_3$  and  $\text{HO}_2$  or react with other more abundant  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_3$  etc. Third, if  $\text{HSO}_5$  did react with a peroxy radical, why should we think that this would lead to a stable nucleating particle?

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: 554–559 (2002).

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.

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

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