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Atmospheric Chemistry and Physics Discussions

Interactive comment on "SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications" *by* et al.

Anonymous Referee #3

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It has been shown that atmospheric nucleation occurs at much lower H2SO4 concentrations than binary or ternary H2SO4 nucleation would predict. Classical binary nucleation might be sufficient to explain nucleation at altitudes of a couple of km (i.e. free troposphere), but the theory fails to explain observed nucleation rates in the boundary layer where nucleation occurs at rates orders of magnitude higher than predicted by classical binary nucleation theory. The reasons for this behavior is yet unknown, and this article provide a synthesis of laboratory and field experiments that allows the authors to formulate a hypothesis regarding some apparent paradoxes found in the body

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of data.

The main idea driven by the authors is that some other species than H2SO4 is responsible for the formation of the initial clusters and hypothesizes that this species might be HSO5 radicals. The authors largely base this conclusion on laboratory experiments were it have been shown that H2SO4 generated from an evaporating liquid require far higher concentrations to nucleate (agreeing with and thereby suggesting a classical binary nucleation pathway) as compared to H2SO4 generated directly in the gas phase. These results do suggest that the gas phase oxidation of sulfur dioxide include a more or less unknown reaction pathway that may lead to the formation of sulfur radicals, suggest by the authors to be HSO5. This path was originally suggested by Friend et al. (1980) and tentatively/indirectly supported by Stockwell and Calvert (1985) and Wayne (1991) based on the fraction regenerated HOx radicals. Still however, additional studies are required to verify this pathway.

The authors also speculate about the pressure dependency of the radical formation. Based on laboratory experiments and ambient observations, the authors suggest this mechanism to be dominant only at low altitudes (high pressure, large availability of stabilizing inert molecules), explaining why the classical binary pathway seems to explain nucleation in the free troposphere while not in the boundary layer.

The argumentation is well built and the speculations presented are well formulated and points towards and alternative particle formation pathway that deserves further investigation. However, still many open question remains. The main problem is that the suggested nucleating species have never been observed, which limits the suggestions presented in the paper.

Although the article of course is speculative, I do not see any apparent problems with speculations of this kind as long as they are well built. New particle formation is one of the greatest challenges in determining the role and response of aerosols in the changing climate system. The results presented here are naturally not conclusive, but

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Interactive Comment

they provide a basis for further discussions and investigations. New approaches and eye-openers are required to move the discussion forward. The article is further well written, both in terms of language and structure. Therefore I recommend publication of the article in its current form.

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