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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation" *by* P. Paasonen et al.

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This paper examines nucleation and grow measurements collected at four European sites and attempts comparison with various theoretical models for new particle formation that have been proposed. There is comparison with the activation model and with the kinetic model, but surprisingly no discussion of the thermodynamic nucleation models even though these generally have the best agreement with laboratory measurements (e.g. the measurements of Zhang and co-workers on several ternary acid-water-organic systems).

In the activation model, formation of a nucleated particle is triggered by attachment of a single sulfuric acid molecule to activate a pre-existing, sub-2nm precursor particle.

Here the nucleation rate would be linearly proportional to sulfuric acid concentration (at steady state) but one wonders why the population of precursors is not included as a potential contribution to the growth rate so as to exclude them from interfering with the author's indirect estimates of contributing organics.

In the kinetic model, the nucleation rate is proportional to sulfuric acid concentration squared. This is a viable model under the assumption that additional, as yet unidentified, components contribute to critical nucleus formation. The kinetic model cannot explain laboratory measurements of binary sulfuric acid-water, or the ternary measurements mentioned above. For these the thermodynamic model does a better job.

The authors show the usual log-log plots of nucleation rate versus sulfuric acid (or organics) concentration from which one can try to infer something about the number of molecules of sulfuric acid (or organics) present in the critical nucleus via the nucleation theorem. Such inference should proceed with caution: It is important to mention that n-theorem arguments (more implicit than explicit in the present work) require a steady state nucleation rate. Otherwise such log-log plots are incapable of shedding light on nucleation mechanism. Thus the thermodynamic models with higher numbers of sulfuric acid in the critical nucleus (e.g. 4-10) are not ruled out. Similarly, several of the author's log-log plots, when focusing on measurements from the individual field sites, do indeed show higher rate sensitivities than would be consistent (under the steady state assumption) with either the activation or kinetic models.

The authors present their results for a simplified model in which nucleated particles are produced at the 2nm diameter detection limit instead of at 1.2 nm, which is their estimate of the critical nucleus size. This simplification excludes the influence of nucleation and growth as coupled processes contributing jointly to the formation of the smallest particles of analysis size. Toward the end of the paper the authors note this weakness and mention calculations they have done along these lines. It would be better to lead off with the calculations showing contributions from both nucleation and growth to 2nm particle formation.

The inference of organic contribution to growth is highly indirect and the models (I have touched on only two of them - not mentioning the organics and their combinations/permutations with the first two models) are speculative and incomplete (comments of previous paragraph). The data is noisy and the reported correlations are weak. It is not clear what if anything atmospheric modelers will be able to take from this paper beyond what is already present in the literature to improve the representation of new particle formation in their models. Nor is it made clear how this paper contributes to scientific understanding of new particle formation. The argument that there are no direct measurements of the contributing organics to new particle formation, made in support of their indirect estimate from growth rate, while probably true, doesn't provide solace.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11795, 2010.