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Atmospheric
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Discussions

Interactive comment on “SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation – Part 1: Laboratory investigations” *by* T. Berndt et al.

T. Berndt et al.

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The authors thank referee 1 for the comments. Replies are given below:

The language and the statements are sometimes strong (possibly calling for copy editing).

Reply: We agree to the opinion of referee 1. In the revised manuscript some "too strong statements" have been corrected.

The key to the different behaviour of H2SO4 formed by evaporation from that formed by oxidation is clearly the chemistry, where the liquid-phase reactions (so-called heterogeneous reactions) or real surface reactions most probably play a decisive role.

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Interactive Discussion

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Even though the chemistry is discussed in detail, the reviewer feels that the reference to the excellent chapters by Finlayson-Pitts and Pitts (2000) should be separated for gas-phase and liquid-phase chemistry and that the original publications and even earlier work might be discussed in addition. Aerosol formation is a known impediment in industrial chemistry of sulphuric acid production, where the rapid uptake of SO3 by concentrated H2SO4 has been explained by the intermediate H2S2O7. The books by Warneck (Chemistry of the Natural Atmosphere, 1988 and 2000) and Heicklen (Atmospheric Chemistry, Academic Press, 1976) and the original work cited therein might be consulted.

Reply: That is a very good remark, thank you very much! In liquid phase SO2 can be efficiently oxidized by O3 or H2O2 depending on pH. Applying the liquid phase results to freshly nucleated particles, for acidic conditions, especially oxidation of SO2 by H2O2 can take place accelerating the growth process. This topic is now discussed in the revised version of the manuscript. It is correct that the industrial H2SO4 process suffers from aerosol formation. Direct hydrolysis of gaseous SO3 is less efficient. Because of the high heat of reaction, a corrosive mist is formed instead of a liquid. Therefore, first SO3 is leached out by H2SO4 producing di-sulphuric acid (at least partly depending on the ratio SO3 / H2SO4). In a subsequent step, hydrolysis of liquid H2S2O7 (SO3/H2SO4) yields H2SO4. In the manuscript there will be no link to the industrial process.

Since the purities of the gases and chemicals are major concern of such study on H2SO4 nucleation, the stated (and possibly unwise, since its definition may be based upon the hydrocarbon traces detectable by a GC with flame ionisation detector) extreme purity of synthetic air should be supplemented by the principle and properties of the Gate Keeper. The purity of the SO2 and the ppm-mixtures of SO2 in N2 then need to be discussed as well. Would it be feasible to generate SO2 by reduction of H2SO4 vapour from the same reservoir? This argument of limited purities holds for the O3 as well, that would react with any wall contaminants and polymer tubing and plasticizers/additives of Teflon tubing and gaskets to bring volatile organics into the system.

Reply: An explanation of the principle of GateKeeper has been added in the Experimental section. Regarding the purity/impurities from the SO2 calibration gases, different SO2 mixtures with different SO2 content were used. Measured total particle numbers varied not more than a factor of 2 or less (mostly) changing the SO2 source. Experience suggests that the experiment should be done as simple as possible. All additional procedures can lead to additional impurities or increased background particle numbers. E.g., in experiments starting from SO3, at the entrance of the flow tube, SO2 was catalytically oxidized to SO3. Commercially available V2O5 catalysts used in industry yielded clearly increased background levels of small particles arising from abrasion of the catalyst itself without any reactions of SO2. So, any procedures of SO2 generation from H2SO4 (if possible for our approach) can lead to a lot of experimental trouble. It should be a good choice to use high purity SO2 from calibration gases. Significant contributions of background impurities or of their oxidation products to H2SO4/H2O nucleation in our experiment are unlikely. In experiments with H2SO4 from the liquid reservoir, cf. fig.2 and fig.6 of this manuscript, detected particle formation is roughly in line with that what was expected from binary H2SO4/H2O nucleation and there are no indications for additional species enhancing nucleation rate (like aromatic acids, cf. Zhang et al., Science 2004). Switching on O3 and subsequent UV and starting HOx chemistry (in absence of SO2!), impurities are oxidized at least partly. In the figures it is clearly seen that for these conditions the particle number remains unaffected. A paragraph is added in the manuscript discussing the possible role of impurities.

In figure 2, the particle number density from H2SO4 vapour shows a constant, exponential increase, not having reached the limiting value on the time scale of the illustration. On the other hand, the particles disappear immediately after switching H2SO4 off. This indicates rapid loss processes acting against a slow saturation of surfaces. So it might be interesting to monitor the increase of particle number density over several days or even weeks. What is the explanation for this exponential(!) increase ("2 to 3 particles cm(-3) after more than 5 h") that must be quite far from steady state?

Reply: Even after a period of days we got no "final" values. The number did not increase continuously; there was also a "going down" from time to time. Obviously, surface effects do strongly influence resulting particle number, at least in our experiment. The reviewer is correct that the observed behaviour is interesting. However, we don’t think that the results gained by the investigations suggested by the reviewer would influence or change the conclusions drawn from the paper. Therefore, at present, we consider these investigations beyond the scope of this paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9761, 2008.

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