

Final response to the referee comments

MS No.: acp-2013-277

We thank the reviewer for the helpful remarks on our manuscript. Please find our point-by-point responses below.

Referee 1:

1. The manuscript would benefit from additional discussion on how the results relate to previous work and which results or techniques are novel. For example, the nucleation enhancement of amine compounds is not a new result, and the additional H<sub>2</sub>SO<sub>4</sub> formation, likely from stabilized Criegee intermediates, has recently been published. The experiments and results reported in this manuscript are interesting, but the novelty is not very clear in its current version.

Reply:

Yes, the referee is right. It's certainly not new that amines enhance atmospheric H<sub>2</sub>SO<sub>4</sub> nucleation and that sCI + SO<sub>2</sub> produces also H<sub>2</sub>SO<sub>4</sub> beside the well-known OH + SO<sub>2</sub> reaction. Using the same experimental setup, the aim of this work was to quantify for close to atmospheric conditions how both, amines and organic oxidation products, may enhance atmospheric nucleation (as given in the title). Such a "comparative study", bases vs. amines, has not been done for all reactants featuring atmospheric concentration levels. This will be explicitly mentioned in the revised version of the manuscript.

2. The authors conclude that organic oxidation products (from alpha-pinene and limonene) alone do not enhance nucleation or contribute to early particle growth. This seems to be inconsistent with numerous environmental chamber studies in which secondary organic aerosols (i.e. particles) are formed from ozonolysis of alpha-pinene without the addition of H<sub>2</sub>SO<sub>4</sub>. The authors should address these potentially conflicting results. Could the difference be due to different generations of oxidation, i.e. do SOA formation experiments go to later generations? As evidence for lack of growth the authors mention that the particles are always detected in the same size bin. It would be appropriate to report more information here, for example, which size bins were measured. It may also be appropriate to report size distributions.

Reply:

We observed no clear indication for any contributions to nucleation of organic oxidation products from the chosen alkenes (in our time window and atmospheric concentrations of the reactants!). It doesn't mean that especially for longer reaction times (formation of organic products of the second, third, ... generation) other processes governed by organic oxidation products could take place and significantly influence new particle formation and or growth. It's a bit speculative at the moment how effective such processes are on a global scale in comparison with the base-mediated H<sub>2</sub>SO<sub>4</sub> nucleation. Our results with respect to the findings of Zhang et al. (Science, 304, 1487-1489, 2004) and Metzger et al. (P. Nat. Acad. Sci., 107, 6646-6651, 2010) are already discussed in the manuscript.

Our findings for the "pure" organic nucleation are not in clear contradiction to results from other studies. In chamber runs a delay time is often observed before newly formed particles are detected. This delay time is much longer than our residence time. Furthermore, it's not clear whether the used

gases in the chamber experiments were clean enough to fully rule out base-mediated H<sub>2</sub>SO<sub>4</sub> nucleation for long reaction times, see also J. Wildt et al., Atmos. Chem. Phys. Discuss., 13, 25827-25870, 2013. Growth of H<sub>2</sub>SO<sub>4</sub> particles due to organic oxidation products: Particle growth by organics is obviously not effective enough to show measurable effects within a growth time of about 50 sec and close to atmospheric levels of organic oxidation products. Riccobono et al. (Atmos. Chem. Phys., 12, 9427-9439, 2012) reported growth rates of about 2 nm/h for 1.5-2 nm particles due to oxidation products of  $\alpha$ -pinene for a  $\alpha$ -pinene conversion rate of 1-6 ppt/sec,  $(2.5 - 15) \cdot 10^7$  molecule cm<sup>-3</sup>s<sup>-1</sup>). The  $\alpha$ -pinene conversion rate stands as a proxy for the formation rate of organic products participating in the growth process. For our  $\alpha$ -pinene reaction rate of  $(0.2 - 2.9) \cdot 10^7$  molecule cm<sup>-3</sup>s<sup>-1</sup> we can assume the reported growth rate of 2 nm/h for small particles as an upper limit. For a 50 sec growth time a diameter increase of 0.028 nm (upper limit) follows, which is very small and impossible to detect. Therefore, our observation is not in contradiction with other experimental findings. This topic will be explained in more detail in the revised version of the manuscript.

3. Regarding the organic oxidation products, which as stated by the authors are primarily first-generation, the authors should address the relevance of their work to atmospheric conditions where oxidation proceeds to later stages of oxidation.

Reply:

Our results are indicative for first generation reaction products not influencing new particle formation and growth processes. However that does not imply that for longer time scales and under atmospheric conditions, higher generation reaction products may affect the nucleation and growth processes. A corresponding discussion will be added to the manuscript.

4. Wikipedia should not be used as a reference. The two references to Wikipedia currently in the manuscript should be replaced by references to scientific publications.

Reply:

We agree to referee's opinion that a web link is not an appropriate reference. In the case of the link to Wikipedia "proton affinity" we will refer to another publication. For the NILU report "Worst Case Studies on Amine Emissions from CO<sub>2</sub> Capture Plants. Norwegian Institute for Air Research. Project Report. 2009." by Karl et al. we will refer to this report directly.

5. The abstract is rather long and the conclusions are very similar to the abstract. I suggest shortening the abstract if possible and rewriting the conclusions, potentially by emphasizing the novelty of the work (see comment 1).

Reply:

Due to referee's suggestions we will shorten the abstract and rewrite the conclusion in light of the comments of both referees and the changes in the text.