**Atmospheric
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Discussions**

Interactive
Comment

Interactive comment on "Effect of NO$_x$ level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes" *by* N. L. Ng et al.

N. L. Ng et al.

Received and published: 12 September 2007

We thank the reviewers for their comments. We have made changes to the text to address these comments. All changes made are minor, and they do not change the conclusion of the manuscript. Responses to specific comments are given below.

Responses to comments by reviewer 1:

1. Some of the terpene concentrations used in these experiments are very low, 5 ppbv or less, which corresponds to a vapor pressure of approximately 4 x 10-6 torr. This is in the semi-volatile range. I could imagine compounds condensed on the walls of the chamber from previous experiments having similar vapor pressures and thus contributing to the VOC loading. Have experiments been performed without added terpene but with all other components (seed particles, oxidant, etc.) in order to determine back-

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Discussion Paper

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ground contributions to SOA mass?

We did not perform blank experiments for these terpene experiments, however, the chambers were baked and flushed continuously for 24 hours under irradiation between experiments. Before each experiment, the chamber air was sampled to ensure that the particle number concentration, O3, and NOx concentrations were below detection limit and that the background air was free of VOCs. Therefore, it is not expected that there would be contribution to SOA growth from compounds coming off the chamber walls. It is also noted that we performed blank experiments for isoprene photooxidation experiments in which the experimental protocols were similar to the current study, and no aerosol growth or artifacts in the mass spectrometry data were observed (Kroll et al., 2006; Surratt et al., 2006).

2. In Table 6 there are two compounds listed with molecular formulas containing 12 carbon atoms. The parent terpene, a-pinene, only has 10 carbon atoms. Also, in Table 7 there is one compound listed with a molecular formula containing 16 carbon atoms and 13 compounds with 17 carbon atoms. The parent terpene, longifolene, only has 15 carbon atoms. Are these thought to be oligomers or could the formulas be wrong?

The compounds are indeed oligomeric (i.e. dimeric) compounds and the formulas are not incorrect. We are confident that these are dimers due to the exact mass data being well within acceptable errors (+/- 2 mDa), as well as the tandem MS data revealing neutral losses of acetic acid (60 Da). The observed neutral losses of acetic acid suggest that particle-phase organic esterification reactions occurred. These reactions would add two additional carbons to a C10-hydroxy-a-pinene and a C15-hydroxy-longifolene oxidation product. The same would occur for a C14-hydroxy-longifolene oxidation product; thus, explaining the observation of C16 compounds in the particle-phase. Similar products were previously characterized in isoprene high-NOx SOA (Surratt et al., 2006) when using similar reaction conditions (i.e. OH radical source as well as dry conditions) of the present study. The dry conditions (low RHs) enhance the formation of particle-phase organic ester products. To clarify, the following sentences are added in Section

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4.2:

"For both a-pinene and longifolene, compounds with more carbon number than the parent hydrocarbon are observed. Tandem MS data for these C12, C16, and C17 acidic organic nitrates reveal a common neutral loss of 60 Da, which possibly corresponds to an acetic acid monomer. Surratt et al. (2006) and Szmigielski et al. (2006) recently showed that particle-phase esterification occurs in isoprene SOA formed under high-NOx conditions. The observed neutral loss of 60 Da for these acidic organic nitrates suggests that these compounds may be dimers formed by particle-phase esterification."

3. Figure 8: In the bottom panel I suggest using the same -100 to +100 Percentage Change scale used in Figure 9 so the two figures can be visually compared more easily.

The percentage change scale in both figures is changed as suggested.

Responses to comments by reviewer 2:

1.Experimental Section. Wall-loss coefficient is very crucial for smog chamber experiments, and it could vary from experiment to experiment. In this study, the author apparently utilizes a set of size-dependent wall-loss coefficients obtained from different experiments using inorganic particles. Are these coefficients appropriate for this study in which particles are organics or covered by organics? Although I understand that this study is to compare the trend of aerosol formation under varying conditions instead of obtain accurate aerosol yield, the accuracy of the wall-loss coefficient may not be important.

All aerosol growth data presented are corrected for wall loss, in which size-dependent coefficients determined from inert particle wall loss experiments are applied to aerosol volume data. The size-dependent wall loss coefficients are determined by atomizing ammonium sulfate particles into the chamber and measuring their decay over time. We assume that once a particle is lost to the wall by diffusion, it will be permanently

deposited on the chamber wall. Such processes should be independent of the composition of the particles and so the wall-loss coefficients determined from inorganic particles are applicable to the organic particles in the experiments. We perform wall-loss experiments frequently (~ every 3 months), and the size-dependent coefficients determined from all the wall loss experiments performed over the last few years agree well.

2. How is the concentration of H_2O_2 calculated? If the H_2O_2 is calculated based on the chamber volume and the liquid volume injected, the result may not be accurate. Because H_2O_2 could be lost to the wall during the injection, it is likely that the actual concentration of H_2O_2 will be much lower. The concentration of H_2O_2 in the chamber is estimated to be ~3 to 5 ppm, based on the rate of hydrocarbon decay and literature values of sigma(H_2O_2) and $kOH+H_2O_2$. To clarify, the sentence "About 3 ppm H_2O_2 is introduced into the chamber (prior to introduction of seed particles and parent hydrocarbon) by bubbling air through a 50% H_2O_2 solution for 2.5 h at 5 L/min." is changed to

"H_2O_2 is introduced into the chamber (prior to introduction of seed particles and parent hydrocarbon) by bubbling air through a 50% H_2O_2 solution for 2.5 h at 5 L/min. The concentration of H_2O_2 in the chamber is not measured; based on the rate of hydrocarbon decay and literature values of sigma(H_2O_2) and $kOH+H_2O_2$, we estimate [H_2O_2] to be ~3 to 5 ppm (Kroll et al., 2006)."

3. In section 5.2.2, the author states that in the intermediate NOx experiments, NO will be consumed quickly and then the aerosol will be a mixture of the products formed under both high and low-NOx conditions. However, at the time the NO concentration approaches zero, only a very small amount of a-pinene should be left for the low-NOx reaction. In addition, O3 level is negligible under both high and low-NOx conditions, while there is considerable amount of O3 formed during the intermediate NOx experiments. NO3 radical levels should also be much higher during the intermediate NOx experiment. The gas-phase reactive oxidation products may further react with O3 and

NO3 radical to form compounds with low volatility that can condense on aerosols. In Figure 1, only the growth curve of intermediate NOx experiment shows a clear "hook", which could be a good evidence to support the further reactions between reactive oxidation products and O3 and NO3 radical. Thus, the compounds of SOA from intermediate NOx experiments may be quite different from those formed from low and high-NOx experiments.

We thank the reviewer for raising this issue. In the original manuscript, It was stated that "In the intermediate NOx experiments, the NO concentration goes to zero about 30 min after the commencement of photooxidation, owing to the rapid reaction of NO and peroxy radicals (HO2 and other peroxy radicals)." To be more accurate, NO concentration approaches zero in 20 min and so the sentence is changed to

"In the intermediate NOx experiments, the NO concentration goes to zero within 20 min after the commencement of photooxidation, owing to the rapid reaction of NO and peroxy radicals (HO2 and other peroxy radicals)."

In the intermediate NOx a-pinene experiment, there is still about 50% of the initial a-pinene remaining at the time when the NO concentration approaches zero and so the final SOA formed can be a mixture of the products formed under high- and low-NOx conditions. We agree that there may be further chemistry between reactive products and O3 and NO3 radical. However, it is unlikely the hook in the intermediate NOx experiments arises from these further reactions. SOA formation from the photooxidation of a-pinene and longifolene has been studied in Ng et al. (2006) using HONO as an OH precursor. Those experiments are similar to the intermediate NOx experiments in this study (except that in this study there is much more HO2 in the system), as NO approached zero and consequently O3 (and NO3) was formed. No hook was observed in the growth curves for a-pinene and longifolene in that study, indicating that further reactions between reactive oxidation products with O3 and/or OH and NO3 radicals do not contribute SOA growth after all the initial hydrocarbon was consumed.

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4.Page 10140, line 11, a-pinene should be longifolene.

Corrected.

5.Figure 1, 2 and 3, captions, why are these curves called time-dependent growth curve? I don't see any time presented in these figures.

Each of the curves in these figures shows the aerosol growth data for a single experiment over the course of the experiment and so they are referred to as "time-dependent growth curves". This term was first introduced in Ng et al. (2006). To clarify, the following sentence is added in Section 3.1 where this term is first mentioned:

"The curves are referred to as "time-dependent growth curves" as each curve represents aerosol growth data for a single experiment over the course of the experiment (Ng et al., 2006)."

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10131, 2007.

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