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Discussions

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Interactive comment on "Low-volatility compounds contribute significantly to isoprene SOA under high-NO conditions" *by* Rebecca H. Schwantes et al.

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Thank you for the helpful comments and suggestions. We appreciate your time for reviewing our paper. We have addressed all of your comments as detailed below:

Comment: p2 line 29: The authors may want to consider the publication of Peeters et al. PCCP 2014, if they mention new gas-phase chemistry of isoprene.

Yes, good point, we had included the Wennberg et al., 2018 review paper as a summary of these advances in gas-phase chemistry, but to be more thorough we have added the following to include some examples of both recent and important experimental and

theoretical studies. We assume you are referring to the Peeters et al. PCCP 2009 and Peeters et al. J. Phys. Chem. A., 2014 papers.

"Additionally, there have been major recent advances in our understanding of isoprene gas-phase oxidation (Wennberg et al., 2018, and references therein) including theoretical (e.g., Peeters et al., 2009, 2014; Kjaergaard et al., 2012) and experimental (e.g., Teng et al., 2017; Nguyen et al., 2015; Lee et al., 2014; Jacobs et al., 2014) studies. This improved understanding of isoprene gas-phase chemistry influences the processes governing isoprene SOA formation and informs the experimental design of the present work."

Comment: p3, Fig 1: I would suggest to add reference for the chemical scheme that is shown. What is the importance of the 1,5-H shift reaction that is shown in the scheme for conditions of high NO in these experiments?

Yes, we added a reference for both Figure 1 and Figure 2 and we removed the peroxy radical undergoing a 1,5-H shift to Figure 1. We do not detect the organic nitrate from this reaction, which is likely because this 1,5-H shift will not occur at the high levels of NO in these experiments. For clarity, we also add further detail describing Figure 1 in the introduction.

In the Figure 1 and 2 caption: "largely based on schemes in Wennberg et al. (2018)"

And in the introduction: "The formation of some organic nitrate SOA-precursors are summarized in Figure 1, which is largely adapted from schemes presented in Wennberg et al. (2018) with the exception of the isoprene dihydroxy nitrooxy alkoxy radical 1,5 H-shift. Wennberg et al. (2018) suggests the importance of a similar peroxy radical 1,5 H-shift, which will not form in the present experiments due to the high levels of NO. However, based on past studies largely on alkane oxidation (Orlando et al., 2003; Atkinson, 2007), the equivalent alkoxy radical 1,5 H-shift is expected to occur and has the potential to form low-volatility nitrates as further described in Section 5.1."

Comment: p5 l6: I assume the specification of the Milli-Q water is meant to be 18 M Ohm.

Yes, thanks we have updated this to "ultrapure water (18 M Ohm, Millipore Milli-Q)"

Comment: p5 l18: I would suggest to add the mean diameter of the seed aerosol for information.

Yes, this has been added: "The seed aerosol particle number concentration had an approximately lognormal diameter distribution centered on average ~100 nm."

Comment: p7 l13: The author mention that in only few experiments NO2 was directly detected and in other NO2 was modelled. How was the model-measurement agreement of NO2 in the experiments, when NO2 was measured?

Yes, unfortunately the luminol NO2/acyl peroxynitrate analyzer, which has less interferences than the Teledyne NOx analyzer was not operational for all experiments. In Figure S3, we show an example of a LV and 2MGA pathway experiment for modeled and measured NO2. The NO2 is reasonably well captured by the model, but as is explained in the supplement remaining biases are likely caused by measurement interferences or unaccounted for wall deposition of NOx reservoir species. We had added reference to this Figure in Section 3 of the main text, but we also now reference this Figure in the instrument section as well:

"The NO2 measured by the luminol NO2/acyl peroxynitrate analyzer compares reasonably well with the simulated NO2 from the kinetic model (Figure S3)."

Comment: p8 l26: I would suggest to mention the parameters that were constrained by measurements in the model.

Yes, this has been added: "As listed in Table 1, the kinetic model was initialized for each experiment with the measured initial concentration of VOC, NO, NO2, and CH3ONO as well as the measured average temperature and relative humidity."

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Comment: p12 l1-9: What does the unreasonable result of the correction of DMA data for wall loss mean for the uncertainty of yields determined for similar conditions in this work?

The unreasonable result of the correction of DMA data described in this paragraph only applies to humid experiments and is why we do not report any DMA data from the humid experiments. We add the following to this paragraph to make this clearer.

"Thus, in this work, only the AMS results will be discussed for the humid experiments and SOA yields are only reported for experiments performed under dry conditions (Table 1). None of the dry experiments exhibited the odd behavior observed in the humid experiments, and the AMS results confirm that under dry conditions minimal nitric acid partitioned to the aerosols (Figure S10). For the dry experiments, the uncertainties are well characterized by the dry control experiments presented in Figure 3."

Comment: p14: Fig 5: The figure does not very clearly support the statement that SOA mass yield depends on the initial seed aerosol correction. There are essentially two values for the range from 1000 to 2000 and from 2500 to 6000 um2/cm3. Could you please comment?

Yes, we have rephrased this in the text to be clearer and offer some further explanation. We interpret Figure 5 as having three regions: 0, 1000-1500, and 2500-6000 um2/cm3 instead of the two you specify. As seed aerosol increases, the SOA mass yield increases until a plateau is reached. This non-linear nature is expected especially for the isoprene SOA precursors as described below:

"Similar to previous studies (e.g., Zhang et al. (2014)), at a certain point increased seed surface area no longer substantially impacts the SOA yield (i.e., Figure 5 after 2500 um2 cm-3). This point will heavily depend on the system and the saturation mass concentration (C*) of the SOA precursors. As shown in Table S2, the isoprene SOA precursors are mostly classified as IVOCs and SVOCs (Donahue et al., 2012). Reaching a point where most of the vapors are in particles relative to the chamber wall

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is expected for IVOCs and SVOCs, which have moderate vapor wall losses in Teflon chambers especially under dry conditions (Zhang et al., 2014; Huang et al., 2018)."

Comment: p25 l27-30: Does the statement that SOA from the LV pathway is moderately higher than from 2MGA takes into account the differences in the turnover of the OH oxidation of the precursors of the two pathways?

Yes, this is exactly why we do not directly compare the measured SOA yields from the LV and 2MGA pathways. As described in Section 5.5, we use the kinetic model at atmospheric conditions to estimate the contribution of both the LV and 2MGA pathways to the total. We have also added the following two sentences to make this clearer:

"In this study, direct comparison of the results from the 2MGA and LV pathways is difficult due to the difference in the extent of oxidation between the two regimes caused by the use of different VOC precursors and the variation in OH levels (Table 1). Thus, the kinetic model is used here to estimate the contribution of each pathway to the total under consistent oxidant levels."