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Interactive comment on “Organic nitrate and secondary organic aerosol yield from NO₃ oxidation of β -pinene evaluated using a gas-phase kinetics/aerosol partitioning model” by J. L. Fry et al.

J. L. Fry et al.

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We thank the reviewer for constructive comments on our manuscript. Below we describe our efforts to address each of the reviewer comments and answer questions.

Reviewer Comment: 1. Page 18047, first paragraph, and elsewhere in the text: It is stated that the NO₂⁺/NO⁺ ratios observed here are very different than those for inorganic nitrate. My understanding is that the AMS quantifies the inorganic nitrate mass by using a calibration relationship that involves the NO⁺ and NO₂⁺ signals and the mass of ammonium nitrate obtained from running pure ammonium nitrate. It sounds like you are quantifying what you call aerosol organic nitrate using the same calibration.

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Please explain this further.

Response: Indeed the quantification of the aerosol organic nitrate is based on the inorganic NH_4NO_3 calibration. As found by Aiken et al (Aiken et al., O/C and OM/OC ratios of primary, secondary, and ambient organic aerosol with high resolution time-of-flight aerosol mass spectrometry, ES&T 42, 4478-4485, 2008), the N/C ratio measured with high resolution aerosol mass spectrometry fit well to the actual N/C ratios of laboratory standards. There are to date no published data on high resolution aerosol mass spectrometric results of the organic nitrates proposed to contribute to SOA in the experiments presented here. In order to make this more clear to the readers we will add the following sentence in the revised manuscript to the AMS experimental description on page 18047: " The quantification of the nitrate content of the SOA was performed based on calibrations with NH_4NO_3 aerosol."

Reviewer Comment: 2. Page 18048-18055: In the kinetic model and throughout the manuscript there is no mention of the potential effects of heterogeneous reactions of NO_3 radicals with SOA particles. Moise et al. [J. Geophys. Res. 107 (2002)] measured a reactive uptake coefficient of approximately 0.003 for the reactions of NO_3 radicals with alkanes. Perhaps this H atom abstraction reaction is the source of excess HNO_3 and long-term changes in particle composition/volatilization observed here. Bertram and co-workers have seen similar uptake coefficients and that the reactions can lead to organic nitrates among other products. Since you have aerosol surface area from your SMPS measurements this contribution to the chemistry could be included in the model.

Response: The timescale of organic nitrate formation observed in this experiment suggests immediate formation from gas-phase $\text{NO}_3 + \text{VOC}$ reactions, so we expect the role of heterogeneous reactions in this case to be limited to possible HNO_3 formation. However, we thank the reviewers for this suggestion of an additional organic nitrate source that may be operating in other similar experiments. For HNO_3 production, using the Moise uptake coefficient and our measured peak aerosol surface area of 5 x

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10-6 cm² cm⁻³ gives a lifetime of NO₃ uptake of ~ 2.7 hours. We will add discussion of this, and a reference to the Moise paper, to the revised manuscript.

Reviewer Comment: 3. Page 18048-18055: Recently, Ng et al. [Atmos. Chem. Phys. 8, 4117-4140 (2008)] observed the formation of organic peroxide dimers from gas-phase reactions between nitrooxyperoxy radicals formed in the reaction of NO₃ radicals with isoprene. The formation of low volatility products such as these through similar reactions could explain the nucleation observed here and also contribute to the SOA mass. Although it may be difficult to include this chemistry in the model, its possible relevance and consequences should be discussed.

Response: We thank the reviewer for calling this to our attention. To the revised manuscript we will add text citing Ng et al (2008) and discussing the possibility that the analogous C₂₀ peroxides that would be formed in the beta-pinene dimerization would have very low volatility.

Reviewer Comment: 4. Page 18060: If I understand the assumption correctly, when the vaporizer temperature is reduced to 145C, only organic nitrates evaporate because the vapor pressures of the non-nitrate organic compounds are too low at that temperature. This assumption could be tested by looking at the AMS signal when the temperature is increased back to 395C or 570C. If non-nitrate organics do not evaporate at 145C, then they should accumulate on the vaporizer and a large burst of non-nitrate signal should be observed when the temperature is increased. Was this observed?

Response: Yes, a pulse of organics was observed upon re-heating the vaporizer.

Reviewer Comment: 5. Page 18062: There is experimental evidence showing that nopinone does not form sufficient enol to play a role in these reactions. Winterhalter et al. [J. Atmos. Chem. 35, 165 (2000)] monitored the concentration of nopinone formed from the reaction of b-pinene with O₃ using in situ FTIR and observed that it is constant over about 45 minutes when exposed to 3 ppmv of O₃. If enol formation were sufficient to react nopinone at the low ppbv levels of NO₃ radicals used here, then it would have

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reacted even faster at 3 ppmv of O₃, which it did not.

Response: We thank the reviewer for pointing out the Winterhalter et al paper. We will add reference to and a brief description of this study to our discussing of the non-nitrate condensing organic. Still, in contrast to those O₃ studies, nopinone has not been observed as a product of NO₃ + beta-pinene and our experiments clearly indicate that there must exist some mechanism by which the organics become less volatile. We hope that this paper will spur further product analysis of these NO₃ + monoterpene reactions, since there clearly remain many open questions.

Reviewer Comment: 6. Page 18064-18067: It should be noted that when extrapolating these chamber results to the ambient atmosphere, consideration should be given to possible differences in HO₂/RO₂ ratios in the chamber and ambient atmosphere. As shown by Docherty and Ziemann [Aerosol Sci. Technol. 37, 877 (2003)], this quantity can have a large effect on SOA formation, especially when the RO₂-RO₂ and RO₂-HO₂ reactions involve tertiary peroxy radicals of the type formed from reactions of b-pinene. In chamber experiments [Jenkin, Atmos. Chem. Phys. 4, 1741 (2004)] HO₂/RO₂ ratios tend to be much smaller than in the clean atmosphere [Hanke et al., Int. J. Mass Spectrom. 213, 91 (2002)], so the products of NO₃ reactions in the atmosphere may be nitrooxy hydroperoxides instead of those formed here, as noted by Atkinson [J. Phys. Chem. Ref. Data. 26, 215 (1997)]. This should be included in the discussion.

Response: We thank the reviewer for pointing out another issue that should be addressed in our paper. Our modeling suggests that in this chamber study, about 75% of organic peroxy radicals reacted with other RO₂ radicals, with most of the remaining RO₂ reacting with NO₃, and only <1% reacting with HO₂. In the revised manuscript we will include this information and cite the sources the referee mentions here in our discussion.

Reviewer Comment: 7. Page 18066: Does CARB include SOA as a PM_{2.5} emission,

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or are their values all primary aerosol?

Response: It is our understanding that CARB PM2.5 emissions inventory would include SOA as well as POA.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18039, 2008.

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