

Interactive  
Comment

***Interactive comment on “Organic nitrate and secondary organic aerosol yield from NO<sub>3</sub> oxidation of  $\beta$ -pinene evaluated using a gas-phase kinetics/aerosol partitioning model” by J. L. Fry et al.***

**Anonymous Referee #2**

Received and published: 6 December 2008

General Comments:

This paper reports results of measurements and modeling of SOA formation from the reaction of  $\beta$ -pinene with NO<sub>3</sub> radicals. The experiments were carried out in the SAPHIR chamber with low ppbv levels of the monoterpene and NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>. Total (gas + particle) organic nitrates including PANs, alkylnitrates, and HNO<sub>3</sub> were monitored using a real-time thermal decomposition method with NO<sub>2</sub> detection developed previously by the Cohen group, the aerosol composition was monitored with an Aerodyne HR-TOF AMS, and NO<sub>3</sub> concentrations were monitored using a suite of instru-

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ments. A simple kinetic model was developed to aid in the interpretation of the results, which indicate that organic nitrates and non-nitrate products are both major contributors to SOA formation. Hydroxynitrates and some potential non-nitrate products were proposed to be the dominant components, based on previous studies of the chemistry of these and related reactions. The measured SOA yield was very high, ~50%, and when used in a regional model and for global estimates it was predicted that monoterpene reactions with  $\text{NO}_3$  may contribute significantly to SOA formation at both scales. These are a class of (nighttime) reactions whose potential role in atmospheric SOA formation has not been studied to any significant extent. The present study is carried out with state-of-the-art chamber facilities and measurement methods under near-ambient conditions, which is important since there is a growing body of literature indicating that SOA formation can be strongly influenced by the concentration regime. The study also includes a nice combination of measurements and modeling. The interpretation of the results seems plausible, with a few exceptions that are noted below, and certainly adds to present understanding of these systems. Overall, I think the paper presents useful new results on an important topic in atmospheric chemistry. The manuscript should be suitable for publication in ACP after issues raised in the comments below are addressed.

#### Specific Comments:

1. Page 18047, first paragraph, and elsewhere in the text: It is stated that the  $\text{NO}_2^+/\text{NO}^+$  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  $\text{NO}^+$  and  $\text{NO}_2^+$  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. Please explain this further.

2. Page 18048-18055: In the kinetic model and throughout the manuscript there is no mention of the potential effects of heterogeneous reactions of  $\text{NO}_3$  radicals with SOA

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particles. Moise et al. [J. Geophys. Res. 107 (2002)] measured a reactive uptake coefficient of  $\sim 0.003$  for the reactions of  $\text{NO}_3$  radicals with alkanes. Perhaps this H-atom abstraction reaction is the source of excess  $\text{HNO}_3$  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.

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  $\text{NO}_3$  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.

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?

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  $\text{O}_3$  using in situ FTIR and observed that it is constant over about 45 minutes when exposed to 3 ppmv of  $\text{O}_3$ . If enol formation were sufficient to react nopinone at the low ppbv levels of  $\text{NO}_3$  radicals used here, then it would have reacted even faster at 3 ppmv of  $\text{O}_3$ , which it did not.

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 HO<sub>2</sub>/RO<sub>2</sub> 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 RO<sub>2</sub>-RO<sub>2</sub> and RO<sub>2</sub>-HO<sub>2</sub> reactions involve tertiary peroxy radicals of the type formed from reactions of b-pinene. In chamber experiments [Jenkin, Atmos. Chem. Phys. 4, 1741 (2004)] HO<sub>2</sub>/RO<sub>2</sub> 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 NO<sub>3</sub> 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.

7. Page 18066: Does CARB include SOA as a PM<sub>2.5</sub> emission, or are their values all primary aerosol?

Technical Comments: None

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

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