

## ***Interactive comment on “SOA from limonene: role of NO<sub>3</sub> in its generation and degradation” by J. L. Fry et al.***

### **Anonymous Referee #2**

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This is an excellent paper that should be published after some minor revisions. Specifically, the authors should take note of a relevant study by Zhang *et al.*, *JPCA*, 2006 and they miss the opportunity to calculate the atomic composition of the SOA using the HR-AMS at their disposal.

The Zhang paper addresses limonene ozonolysis and includes a discussion of heterogeneous uptake by ozone to unsaturated limonene-derived SOA as well as interpretation of (unit mass resolution) AMS spectra under low and high NO<sub>x</sub> conditions. Those topics seem germane here. Zhang *et al.* concluded that ozone uptake to limonene SOA is very rapid under low-NO<sub>x</sub> conditions (this was confirmed in the Maksymiuk paper cited by Fry *et al.*) but that it is quite slow under high-NO<sub>x</sub> conditions. Without slow ozone uptake to the SOA in this experiment, it is likely that ozone would rapidly

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scavenge any double bonds available for NO<sub>3</sub> uptake. Thus, on the face of it, these studies appear to be consistent with each other; however, this should be discussed. In addition, Zhang *et al.* make use of PTRMS data to assess the loss of limonene at  $m/z = 137$  as well as the loss of a first-generation product (evidently unsaturated) at  $m/z = 81$  with an apparent ozone rate constant about a factor of 30 lower than limonene. Given the uncertainties in gas-phase chemistry discussed here, it would be nice to see more use of the PTRMS data than simple observation of the limonene loss.

Also, given that the authors invoke additional oxidation as a potential explanation for the discrepancy between predicted and observed SOA levels, it would be very interesting to see a comparison between the bulk atomic composition of the SOA, as observed by the AMS using the relationships discussed by Aiken *et al.*, *EST* 2008, and the atomic composition inferred from the surrogates used to represent the SOA. Is the AMS-derived O:C higher than that of the surrogates? Would adding two carbonyl groups fix this? What about the mean oxidation state of carbon, as proposed by Kroll *et al.* in *Nature Chemistry* this year? Are the surrogate products sufficiently oxidized?

Finally, the dramatic behavior of N<sub>2</sub>O<sub>5</sub> really does require a little more discussion. Assuming that the ozone and NO<sub>2</sub> did not do anything strange during this period, it would seem that some relatively labile reservoir of nitrate may have appeared as an intermediate species (between hours 11 and 16, as discussed by the authors). This is exactly when the total AN peaks, and it is even roughly consistent with the period and magnitude of the discrepancy between the total AN model and the total AN measurements shown in Fig. 6. If one simply takes measurement - model for total AN from Fig. 6 and plots that on Fig. 7, how much of the mysterious divot is filled in?

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 31083, 2010.

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