

Interactive comment on “A product study of the isoprene+NO₃ reaction” by A. E. Perring et al.

Anonymous Referee #1

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This paper describes studies of the product yields from the reaction of NO₃ with isoprene using a combination of PTR-MS and thermal decomposition – LIF instrumentation for product quantification. Some of the authors of this work (and others) have shown that the formation of nitrate species in the title reaction and their subsequent chemistry can exert significant impacts on NO_x budgets and ozone production, and thus studies of this type are clearly useful.

In general, the study appears to be well designed and carried out, the conclusions drawn are sensible, and it is my opinion that the paper warrants publication subject to minor revision as noted below. Given that the yields obtained depend somewhat on relative concentrations of radicals (as the authors themselves point out on pg. 5246), I will note, however, that it would have been nice to see a range of conditions explored, rather than basing the paper on what appears to have been a single experiment. A few questions, comments, and suggestions are listed below.

The concentrations given at the beginning of the Methods section, and those given at the beginning of the Results section do not seem consistent to me. Are perhaps the NO₂ and O₃ steady-state concentrations reversed?

It seems that a couple of the issues identified near the bottom of pg. 5242 (scrubbing of MVK/MACR, thermal decomposition of isoprene) could be tested fairly readily using authentic samples.

Bottom of page 5244 – Comparing the total observed product concentration (about 40 ppbv?) to the isoprene loss (about 30 ppbv?) seems to me to be a more realistic method for calculating the carbon balance and for assessing overall accuracy of the calibration factors and associated assumptions.

On page 5246, line 25, should this read m/z 146, rather than m/z 130?

While I agree with the entire discussion on pages 5247-5248 regarding the yield determination versus N₂O₅ consumption, it seems to me to be drawn out and could be condensed.

I find myself a little confused regarding the uncertainties in the nitrate yields. What uncertainties are actually included in the 65±3% value quoted on pages 5246 and 5248? Where does the roughly 20% uncertainty in the PTR-MS calibrations fit in to this picture? Or the possibility of ions other than m/z 83 contributing, as discussed on page 5245? A clear statement of the overall uncertainty on the yield of nitrates (or more specifically nitrooxycarbonyls) should be made. While I agree that the N₂O₅-based yields are likely a lower limit, are the carbon- and nitrogen-derived yields given on page 5246 really significantly different?

There are a couple of words missing on pg. 5249, lines 9-10, I think - “previously reported value of “, “NO₂ is regenerated”...

Lastly, the authors provide valuable discussion on the possible fates of the nitrooxy carbonyls in the atmosphere. However, can more quantitative statements be made

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regarding the loss of these species in the actual experiment, i.e., can a limit be put on their chemical loss in the chamber and the resulting impact on the reported yield?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5231, 2009.

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