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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A product study of the isoprene+NO_3 reaction" *by* A. E. Perring et al.

R. Cohen

rccohen@berkeley.edu

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We thank both referees for their helpful and constructive comments. Both referees requested a more thorough treatment of the uncertainty in the nitrate yield presented in this manuscript. The stated uncertainty has been modified and text has been added to describe the associated calculation in more detail. All technical corrections noted have been addressed in the revised manuscript and detailed responses to specific scientific comments are addressed below.

Response to Anonymous Referee #1

Reviewer comment: 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?

Response: Yes, the O3 and NO2 concentrations were reversed. Corrected.

Reviewer comment: 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.

Response: These tests were done and no decrease in signal for either Isoprene or (MACR+MVK) was observed as a result of the basic scrubber or thermal dissociation. This likely indicates that the interferences described here are the result of additional compounds at those masses. A statement of the results of these tests are now added to the manuscript.

Reviewer comment: 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.

Response: We have added text at the end of paragraph 2 of the Product Quantification section to discuss the comparison between the isoprene consumed and the products formed and to clarify that the agreement between the two lends confidence to the stated assumptions and calibration factors.

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

Response: m/z 30 is correct as it results from dehydration of the molecular hydroxy nitrate ion at m/z 148. Text has been added to explain the detection of hydroxy-nitrates at this mass.

Reviewer comment: 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.

Response: We have edited that section to make it more succinct.

Reviewer comment: 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.

Response: The originally stated ranges were considering only the confidence interval for the fit parameters. We have edited the numbers to include the instrumental uncertainties, stated the appropriate ranges for the individually derived slopes for each of the PTR-MS and the LIF and recalculated the reported value as an average of the two slopes with the uncertainty determined by the two individual uncertainties. While it is possible that other ions contribute to the m/z 83 signal, the agreement between m/z 83 and the LIF measurement gives us confidence that those interferences are likely small and we do not attempt to quantify them explicitly.

Reviewer comment: 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?

Response: We have amended the text so that the reported yield represents that calculated from the carbon-containing products and that derived from the N2O5 consumption is a lower limit and a piece of corroborating evidence.

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

Response: “Previously reported of +/- 20%” changed to “previously reported (+/- 20%)” “NO2 regenerated” changed to “NO2 is regenerated”

Reviewer comment: Lastly, the authors provide valuable discussion on the possible fates of the nitrooxy carbonyls in the atmosphere. However, can more quantitative

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statements be made 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?

Response: The calculated loss of these compounds is very small due to the fact that isoprene was in great excess at all times. We do not think the conditions in the current experiment allow us to discuss the processing of nitrates derived from NO3+isoprene in the atmosphere but we refer the reviewer to Rollins et al. (ACPD, 2009) where experimental conditions were different and the products of oxidation of isoprene nitrates by NO3 were investigated.

Response to R. Atkinson (Referee #2)

Reviewer comment: Page 5233, line 29. Kwok et al. (1996) did not study the kinetics of the NO3 + isoprene reaction, not provide any data concerning the positions of NO3 addition to isoprene. This reference should be deleted from this sentence.

Response: The reference has been removed from the sentence in question.

Reviewer comment: Page 5240, lines 3 and 4. Based on previous chamber studies of N2O5 behavior (see, for example, Tuazon et al., 1983), a significant portion of N2O5 decaying to the chamber walls appears as gaseous nitric acid (which in turn gradually decays to chamber walls). Hence the overall nitrogen loss rate may be slower than the N2O5 loss rate. This comment is also relevant to the sentence on page 5248, lines 22-24.

Response: We have added the Tuazon reference and amended the discussion of the NOy and N2O5 loss rates.

Reviewer comment: Page 5240, line 29. On page 5235 it is stated that the injection of isoprene took 6 min, versus 5 min stated here. I assume these should be the same times.

Response: Changed.

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Reviewer comment: Page 5243, line 12. I believe that the Kwok and Atkinson (1995) reference should be replaced by Kwok et al. (1995).

Response: Changed.

Reviewer comment: Page 5246, lines 17 and 18. The authors should give more detail about how they derived the upper limits to the total nitrate yields from Figure 3b (by taking the upper bounds of the error bars?)

Response: We have amended the stated range slightly and added text to describe the methods used to arrive at the stated limits.

Reviewer comment: Page 5247, line 15. The rate constant attributed to Barnes et al. (1990) looks as through it is the value from Dlugokencky and Howard (1989) [the Barnes et al. (1990) study was at room temperature only]. IUPAC (2009) provides an evaluated rate constant for NO3 + isoprene, with their current recommendation being very similar to that used in this manuscript.

Response: The reference has been changed from Barnes et al. to Dlugokencky and Howard.

Reviewer comment: Page 5247, lines 28 and 29. The symbols in Figure 4 appear to be different to those stated on page 5247.

Response: Changed.

Reviewer comment: Page 5248, lines 24-26. This sentence is incomplete (especially on line 24), and on line 25 "reaction" should be "react".

Response: “NO3 is likely to. . .” changed to “NO3 is likely lost to. . .reaction with. . .”

Reviewer comment: Page 5249 and 5250. Concerning the reactivity of product species towards NO3 radicals (and OH radicals); in general the presence of an OH group enhances the reactivity towards NO3 or OH radical addition, while the presence of a carbonyl group (-C(O)R or -CHO) decreases the reactivity. For example,

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HOCH2CH=CHCHO is less reactive than 1,3-butadiene towards OH radicals (Baker et al., 2005, Berndt and Böge, 2007), with the reactivity increase due to the OH group being more than offset by the decrease in reactivity due to the carbonyl group. Based on OH radical reactions with alkyl nitrates, the presence of an ONO2 group is also expected to decrease the reactivity towards NO3 radical addition. Hence the carbonyl-nitrates formed from NO3 + isoprene are expected to be less reactive than isoprene towards reaction with NO3 radicals, OH radicals and O3 (as observed by the authors for reaction with NO3 radicals).

Response: The text has been updated to reflect a recent measurement of the reactivity of product nitrates to reaction with NO3 and to reflect the known impacts of functional groups on the reactivity of double bonds.

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

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