

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

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This manuscript reports the results of an excellent and comprehensive study of the products of the gas-phase reaction of NO₃ radicals with isoprene. Reactants and products were monitored in real time by proton transfer reaction mass spectrometry (PTR-MS) and by a thermal dissociation - LIF instrument. A few relatively minor comments which the authors should address are as follows:

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.

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

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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.

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.

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

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?)

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.

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

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

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, 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 to-

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wards 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).

References

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