

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-128

Anonymous Referee #1

Referee comment on "Impact of ozone and inlet design on the quantification of isoprene-derived organic nitrates by thermal dissociation cavity ring-down spectroscopy (TD-CRDS)" by Patrick Dewald et al., Atmos. Meas. Tech. Discuss.,
<https://doi.org/10.5194/amt-2021-128-RC1>, 2021

This paper presents an examination of the temperature-dependent conversion of multi-functional nitrates from isoprene chemistry in TD-CRDS measurement systems. I applaud this group for their continued careful and critical examination of this technique that has been used for many field campaigns by a number of research groups, most of whom have stopped doing this kind of homework long ago. This paper is a very useful follow-on to previous work by this group and should be published pending the authors response to the following general and specific comments.

General Comments

There is no C-N bond in an organic nitrate molecule, nor in a peroxyxynitrate molecule. This appears in several places (lines 300, 313, 371) and is incorrect. It seems the bonds the authors are referring to is the RO-NO₂ bond, which is the weakest bond in the molecule (160-175 kcal/mole), and the RO₂-NO₂, which range from ~88 to 117 kcal/mole.

What does nitryl chloride (ClNO₂) do in your inlets?

Specific Comments

Abstract: Line 15-16. Why not just include a brief description of the solution to the problem, similar to the sentence on lines 540-542?

Line 30. I disagree, NO_3 initiates oxidation of only comparatively few VOCs in the nighttime troposphere, e.g. alkenes, DMS.

Line 43. Isoprene is not the most abundant NMVOC in the atmosphere. Isoprene has the highest total source to the atmosphere, but that is a different thing. The much less reactive small alkanes and some oxygenates are more abundant than isoprene in any but the most biogenically impacted environments in the troposphere.

Line 106. It feels like the phrase 'to acquire complete mixing...' is a bit awkward.

Line 197. Define MPAN somewhere.

Line 231. What were the humidities and NO_2 concentrations used in these tests?

Line 269. Previously, you said the experiments were conducted by allowing the temperatures to decrease from high to low.

Line 277. More efficient compared to what?

Line 295. Monotonic increase with what? Temperature?

Line 311-312. This seems to be a partial sentence, i.e. something is missing here.

Line 315. The addition of the word unambiguously implies that there might be RO_2NO_2 compounds in some isoprene- NO_3 chamber studies, is that true?

Lines 324-325. I assume these are concentrations at the exit of the SCHARK? Otherwise, how does 40.5pptv of $\text{N}_2\text{O}_5 + \text{NO}_3$ make several ppbv of organic nitrates?

Lines 330-335. How long did you wait for the signal to stabilize at each temperature step? How well did it stabilize?

Line 428. The word "exact" is not appropriate here.

Line 469. What is meant by "exchange rate"? Don't you really mean residence time?

Line 475. Can you give an estimate for the O-O bond in typical peroxides?

Line 523-524. You have only circumstantial evidence that the molecule has a double bond or a peroxide group. It could be one or the other since you have only the complex mixture formed in isoprene-NO₃ chemistry to go by, you haven't tested each separately.

Figure 3a. I have a hard time distinguishing the open and closed squares, especially in the 600-650K region of the plot.