

## Reply to Anonymous Referee #1

*In the following, the referee's comments are reproduced (black) along with our replies (blue) and changes made to the text (red) in the revised manuscript. Lines numbers are referring to the unrevised version of the manuscript.*

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.

We thank the referee for the positive evaluation of our manuscript and for the useful 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–NO<sub>2</sub> bond, which is the weakest bond in the molecule (160-175 kcal/mole), and the RO<sub>2</sub>–NO<sub>2</sub>, which range from ~88 to 117 kcal/mole.

Thanks for pointing it out, we are indeed referring to the O-N bond of the mentioned compounds and changed it in the manuscript accordingly:

L301 : [...] several studies have shown that the O-N bond-strength in various alkyl-nitrates [...]

L313 : It seems unlikely that this could have a stabilising effect on the O-N bond in RO<sub>2</sub>NO<sub>2</sub> [...]

L371 : [...] those required to break the O-N bond is the fact that [...]

What does nitryl chloride (ClNO<sub>2</sub>) do in your inlets?

The possible interference of ClNO<sub>2</sub> during the detection of ANs using an inlet very similar to TDI-1 has been discussed in Sobanski et al. (2016). Since the thermograms of iPN and PAN obtained with TDI-2 are very similar to those obtained with TDI-1, we expect comparable results for ClNO<sub>2</sub> using these two inlets. In an further experiment we detected ClNO<sub>2</sub> with TDI-2 heated to 698 K, but did not see any signal additional to NO<sub>2</sub> with TDI-3 heated to 448 K. This confirms that that ClNO<sub>2</sub> is measured in the ANs inlet with TDI-2, but does not interfere with PNs measurements with TDI-3.

We append this measurement as Fig. S7 to the SI and refer to it in the manuscript by adding:

In addition, similar to the observations of Sobanski et al. (2016), ClNO<sub>2</sub> can interfere with the detection of ANs.

The experiment shown in Fig. S7 reveals that ClNO<sub>2</sub> is detected with TDI-2 at 698 K, but not with TDI-3 at 448 K.

### 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?

We replaced the sentence in L15/16 with:

The use of a TDI consisting of a non-reactive material suppresses the conversion of isoprene-derived ANs at 473 K, thus allowing selective detection of PNs. The potential for interference by the thermolysis of nitric acid (HNO<sub>3</sub>), nitrous acid (HONO) and O<sub>3</sub> is assessed.

Line 30. I disagree, NO<sub>3</sub> initiates oxidation of only comparatively few VOCs in the nighttime troposphere, e.g. alkenes, DMS.

We modified the sentence in L33 accordingly:

At nighttime, when OH radicals and NO are significantly less abundant, the NO<sub>3</sub> radical can initiate the oxidation of many VOCs that e.g. contain a double-bond.

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.

We changed the sentence in L43 to:

Isoprene is with a total global emission of  $\approx 500 \text{ Tg yr}^{-1}$  significantly released to the atmosphere (Guenther et al., 2012) [...]

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

We replaced “acquire” with “achieve” in L106:

O<sub>3</sub> measurements were also used to establish the time required (under standard flow conditions) to achieve complete mixing within the chamber (< 1 minute) [...]

Line 197. Define MPAN somewhere.

Done, we added the definition in L197:

Compared to ANs, we expect the mixing ratios of e.g. PAN, O<sub>2</sub>NOCH<sub>2</sub>C(CH<sub>3</sub>)=CHC(O)O<sub>2</sub>NO<sub>2</sub> or methacryloyl peroxyxynitrate (MPAN) in this system to be negligible.

Line 231. What were the humidities and NO<sub>2</sub> concentrations used in these tests?

The values can already be found in the caption of Fig. S2 but are now additionally mentioned in the main text in L231:

In separate experiments, humidified synthetic air (RH = 40 %, 23°C) and NO<sub>2</sub> (10.8 ppbv) were sampled through a PFA line directly to the instrument.

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

This thermogram was also measured from high to low temperature. We rephrase the sentence in L269 to underline that we are not referring to the experimental procedure but aim to qualitatively describe the thermogram:

Conversion of HNO<sub>3</sub> to NO<sub>2</sub> starts at ~550 K and increases with rising temperature.

Line 277. More efficient compared to what?

There is a typo. HNO<sub>3</sub> is converted to NO<sub>2</sub> more efficiently in TDI-1 than in TDI-2. We now write:

The apparently more efficient (~ factor three) conversion of HNO<sub>3</sub> to NO<sub>2</sub> in TDI-1 than in TDI-2 is explained by the loss of NO<sub>2</sub> at high temperatures in TDI-2 through the reaction with O-atoms (see section 3.3).

Line 295. Monotonic increase with what? Temperature?

Correct, we added this missing information to the manuscript in L295:

[...] we observe a monotonic increase in NO<sub>2</sub> with the temperature which is a factor of ~ 2 steeper in TDI-1 than in TDI-2.

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

In fact, this was an unintended relative clause. We removed “which” in L312:

The dominant 1,4-peroxy radical formed when NO<sub>3</sub> reacts with isoprene has a nitrate group separated by two carbon atoms from the peroxy carbon.

Line 315. The addition of the word unambiguously implies that there might be RO<sub>2</sub>NO<sub>2</sub> compounds in some isoprene-NO<sub>3</sub> chamber studies, is that true?

We have removed the word “unambiguously” which, perhaps, was misleading.

Lines 324-325. I assume these are concentrations at the exit of the SCHARK? Otherwise, how does 40.5 pptv of N<sub>2</sub>O<sub>5</sub>+NO<sub>3</sub> make several ppbv of organic nitrates?

The referee’s assumption is correct. To underline this we now write:

The combined concentration of N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> that remains after the reaction with ~ 22 ppbv isoprene (7 sccm of 46.5 ppmv) was measured as 40.5 pptv.

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

The TDI temperature was held for ≈ 20 minutes at each temperature step to record the signal for each of the four O<sub>3</sub> concentrations (0, 47, 104 and 202 ppbv). The signal with 0 ppbv O<sub>3</sub> was measured twice, i.e. at beginning and end of each 20-min-period and was reproducible within 30-150 pptv. We add this to the manuscript:

At each temperature step (periods of 20 min), after recording the signal under O<sub>3</sub> free conditions (black squares), a low (40-54 ppbv, green triangles), medium (97-111 ppbv, blue triangles) and high (185-219 ppbv, orange circles) mixing ratio of O<sub>3</sub> was added in front of the TD-inlets. Before cooling to the next temperature, the signal without O<sub>3</sub> was measured again and agreed within 30-150 pptv to the value at the beginning of the corresponding period.

Line 428. The word “exact” is not appropriate here.

True, we removed it.

Line 469. What is meant by “exchange rate”? Don’t you really mean residence time?

As explained in section 2.1 (L98-102), the exchange rate constant and residence times are related reciprocally. Since such dilution or incoming flows are typically incorporated as a first-order rate into the model, we prefer to stick to “exchange rate”.

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

The bond dissociation energies of organic peroxides typically vary between 45-50 kcal/mol, with tert-butyl hydroperoxide as a representative of an alkyl hydroperoxide having a BDE of ~ 45 kcal/mol (Bach and Schlegel, 2020). The O-O bond is thus expected to be weaker than the O-N of organic nitrates. We now write in L475:

Indeed, hydroperoxides not only have high affinity for surfaces but also have a rather weak O-O bond with a dissociation energy of  $\approx 45$  kcal/mol (Bach and Schlegel, 2020) [...]

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-NO<sub>3</sub> chemistry to go by, you haven't tested each separately.

Right. We emphasize this by changing the sentence in L523/524:

[...] and that this only occurs when the organic nitrate either has a double-bond or a hydroperoxy group (or both).

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

Thanks for drawing attention to this. We revised Fig. 3a accordingly.

### **References**

Bach, R. D., and Schlegel, H. B.: Bond Dissociation Energy of Peroxides Revisited, *J. Phys. Chem. A*, 124, 4742-4751, doi:10.1021/acs.jpca.0c02859, 2020.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model. Dev.*, 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.

Sobanski, N., Schuladen, J., Schuster, G., Lelieveld, J., and Crowley, J. N.: A five-channel cavity ring-down spectrometer for the detection of NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, total peroxy nitrates and total alkyl nitrates, *Atmos. Meas. Tech.*, 9, 5103-5118, doi:10.5194/amt-9-5103-2016, 2016.