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 peroxynitrate molecule. This appears in several places (lines 300, 313, 371) and is incorrect. It seems the bonds the authors are referring to is the $RO–NO_2$ bond, which is the weakest bond in the molecule (160-175 kcal/mole), and the $RO_2–NO_2$, 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_2NO_2 […]

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

What does nitryl chloride ($ClNO_2$) do in your inlets?

The possible interference of $ClNO_2$ 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 $ClNO_2$ using these two inlets. In an further experiment we detected $ClNO_2$ with TDI-2 heated to 698 K, but did not see any signal additional to NO_2 with TDI-3 heated to 448 K. This confirms that that $ClNO_2$ is measured in the ANs inlet with TDI-2, but does not interfee 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), $ClNO_2$ can interfere with the detection of ANs. The experiment shown in Fig. S7 reveals that $ClNO_2$ 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_3), nitrous acid (HONO) and O_3 is assessed.

Line 30. I disagree, NO_3 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_3 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 ≈ 500 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_3 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 defition in L197:

Compared to ANs, we expect the mixing ratios of e.g. PAN, $O_2NOCH_2C(CH_3)=CHC(O)O_2NO_2$ or methacryloyl peroxynitrite (MPAN) in this system to be negligible.

Line 231. What were the humidities and NO_2 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_2 (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_3 to NO_2 starts at ~550 K and increases with rising temperature.

Line 277. More efficient compared to what?

There is a typo. HNO_3 is converted to NO_2 more efficiently in TDI-1 than in TDI-2. We now write:

The apparently more efficient (~ factor three) conversion of HNO_3 to NO_2 in TDI-1 than in TDI-2 is explained by the loss of NO_2 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_2 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_3 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_2NO_2 compounds in some isoprene-NO_3 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 $N_2O_5+NO_3$ make several ppbv of organic nitrates?

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

The combined concentration of $N_2O_5 + NO_3$ 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 $\approx$ 20 minutes at each temperature step to record the signal for each of the four O_3 concentrations (0, 47, 104 and 202 ppbv). The signal with 0 ppbv O_3 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_3 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_3 was added in front of the TD-inlets. Before cooling to the next temperature, the signal without O_3 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_3 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.

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Reply to Anonymous Referee #2

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. Line numbers are referring to the unrevised version of the manuscript.

Dewald et al. examined the conversion of isoprene derived nitrates to NO2 in heated inlets. The isoprene nitrates were generated from reaction of the nitrate radical with isoprene in a large environmental chamber. Three inlet designs were evaluated: a conventional heated quartz tube, common in such instruments, a quartz inlet containing glass beads, and a heated inlet constructed from PFA Teflon. Measurement artifacts arising from the thermal decomposition of ozone (to atomic oxygen) and of nitric and nitrous acid (to hydroxyl radical) were evaluated.

This is a well-written and thorough manuscript. The paper will be of interest to the growing community of TD-CRDS and TD-CEAS users and within the scope of AMT. I recommend publications once the authors have considered my comments below.

We thank the referee for the positive evaluation of our manuscript and for the useful comments.

General comment

The abstract boldly promises a viable solution to broadened thermograms observed in the measurement of isoprene nitrates by TD-CRDS but in the end falls somewhat short of this goal. The proposed solution, a better-performing PFA inlet, is not a viable alternative to current inlet designs since it cannot be heated above ~ 500 K without melting. Perhaps more discussion is needed to better articulate what specific problem this paper ultimately has addressed.

The referee is right, this work presents a pragmatic approach to enable separate detection of PNs and isoprene-derived ANs, but not to suppress broadened thermograms under field conditions. We thus replaced the sentence in L15/16 of the abstract 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_3), nitrous acid (HONO) and O_3 is assessed.

Specific comments

line 1/title: Replace "detection" with "quantification".
Correction made.

lines 15/16. An abstract for a scientific paper should be sufficiently representative of the paper if read as a standalone document. In this spirit, please name the "viable solution to this problem" rather than teasing the reader at this point.
We agree to that and modified the abstract accordingly (see answer to general comment above).

line 108. "by passing a fraction of the air" Is UV transparent material such as quartz used here? Please provide more experimental details.
The air was passed through a cuvette (~ 70 cm³) that is transparent for UV light. We added this information in L108:
O_3 (up to 600 ppbv) was generated by passing a fraction of the air flowing into the chamber through a UV-transparent cuvette (~ 70 cm³) illuminated by a low-pressure Hg-lamp (PenRay) that dissociated O_2 (to O atoms and thus O_3) at 185 nm.

lines 141/143. The temperatures required for full conversion of PN or AN depend on residence time and on where the temperatures are measured and thus are not universal. Please note the dependence of these conversion temperatures on inlet residence time(s) here (they are given on lines 176-177) and add a qualifier such as "In our inlets, ..."
line 142, 143 "results in conversion" and "additional conversion". Should this say: complete conversion?
We agree and underline these two points (non-universality of our conversion temperatures, extent of conversion) by modifying the sentence in L141-143:
At the given conditions (i.e. flow rate, pressure, residence time in the heated section), keeping our TDI at temperatures close to 448 K, results in quantitative conversion of PNs to NO_2 so that the cavity sampling via this inlet measures the sum of PNs + NO_2. Heating our second TDI to ≈ 650 K results in the complete conversion of ANs to NO_2 so that the sum of ANs + PNs + NO_2 can be measured as described in the literature cited in the introduction.

line 162-177. Please comment on (any) pressure drops associated with placing glass beads in the inlet.

The presence of glass beads in TDI-1 leads to a pressure drop of ≈ 23 hPa compared to TDI-1 lacking glass beads. We add this in L166:

The glass beads were supported on a 2 cm thick glass frit and reduce the pressure downstream by ≈ 28 hPa compared to TDI-1.

line 166. Wouldn't the glass bead also lead to more uniform heating of the sampled gas and thus aid in the dissociation of PN and AN?

This is indeed what we would expect and partially explains why TDI-2 produces thermograms of iPN similar to that obtained with TDI-1 despite their different heating section lengths. We already mention this in L221.

line 180/Figure 2. Please state the temperature of the SCHARK chamber. Assuming it is 298K, one would expect with ~4 ppbv of NO2 an equilibrium N2O5:NO3 ratio of ~3:1, as was indeed observed at 11:45. However, the observed ratios at the earlier times (e.g., at 10:45) seem lower than expected from equilibrium. Under the conditions described here, the time to achieve equilibrium should be sufficiently short (minutes). Please comment as to why the N2O5:NO3 deviates initially.

The temperature of the SCHARK was not recorded, but is close to room temperature (296 ± 2 K). The observed change in the N_2O_5:NO_3 ratio in the above-mentioned period (when the chamber was not in steady-state yet) is entirely consistent with an increase in the NO_2 concentration from 3.4 ppbv (at 10:45 LT) to 4.8 ppbv (at 11:45).

line 186 "after subtraction of the N2O5 mixing ratios" - please indicate that you are subtracting N2O5 here in the figure legend and caption and note that you are also subtracting NO2 (I am guessing).

Correct, both NO_2 and N_2O_5 were subtracted from the signal obtained with the TDI-channels. We add this information in the caption of Fig. 2:

Note that the NO_2 and N_2O_5 mixing ratios were subtracted from the organic nitrate signals (middle panel).

line 187 The residual signal is curious. Is it possible NO2 is lost in the low-temperature reference channel to NO2+O3 and N2O5 formation but not in the heated channel?

Given the short residence time in the unheated inlet (0.33 s) and the low rate coefficient of the reaction between O_3 and NO_2 at 298 K (3.5×10^{-17} cm^3 molecule$^{-1}s^{-1}$; IUPAC, 2021) only ≈ 0.1 pptv of 4000 pptv NO_2 would be converted to NO_3 in the presence of 100 ppbv O_3. We thus keep the alternative explanation for the residual signal in L187.

line 194-195. Since the amount of isoprene added (i.e., its concentration) is known (line 202), please calculate the yield of AN relative to integrated amount of NO3+Isoprene.

The concentration of isoprene in flow steady-state in the presence of all reactants was not measured but calculated from the flows and expected consumption by O_3, NO_3 and OH. In addition, the chamber is not characterised for wall loss of ISOP-NIT and due to the long residence in the chamber in combination with the high amounts of O_3, ozonolysis of ISOP-NIT may bias the AN yield determination additionally. For that reason, any AN yield estimated from this would be highly speculative. The sentence in L202 concerning the isoprene concentration is misleading though. To clarify that isoprene concentrations after oxidation are not measured, we modify the sentence in L202:

This is however never the case in the present experiments as isoprene is continuously flowed into the chamber and remains according to model calculations (see below) at a level of ≈ 11.4 ppbv.

line 200 "Very low concentrations" Please be quantitative.

The concentration of isoprene has to be low and the concentration of e.g. aldehydes (or other precursors) high enough so that the reaction of NO_3 towards (usually less reactive) aldehydes becomes competitive to the one with isoprene. The threshold concentration is thus highly dependent on the experimental conditions (i.e. yield of precursors vs. steady-state concentration of isoprene) and not universal. Instead of giving a concentration, we rephrase the sentence in L200:

The formation of PNs only takes place once isoprene has been depleted so that secondary oxidation of the above-mentioned aldehydes by OH or NO_3 leading to further acyl-peroxy radicals (which form PNs) become at least competitive to the primary oxidation of isoprene.

line 201. Consider adding a reaction scheme for clarity.

Considering the minor importance of the very limited routes for PN formation in the dark we prefer not to add a reaction scheme which would distract from the reaction paths we list that are relevant for this work.

line 205-206. "This reaction path is a minor one" How do you know this?

The branching ratios given in Nguyen et al. (2016) imply that the acetyl peroxy radical is formed with a relatively low yield, which is consolidated by the CIMS measurement in Fig. 12. We modify the sentence in L205:

However, according to the branching ratios given in Nguyen et al. (2016), this reaction path is a minor one and $CH_3C(O)O_2$ (and thus PAN) should be formed in negligible amounts.

line 258. Please describe the Iodide-CIMS and how it "was coupled to the experiment" in section 2 "Experimental".
We added a brief description of the CIMS instrument and given the minor importance of the CIMS measurements to this work, we prefer to append it as section S8 in the Supplement rather than in the "Experimental section:

S8 Detection of PAN, HONO and HNO$_3$ with I-CIMS
A chemical ionization mass spectrometer using iodide primary ions (I-CIMS) described recently (Dörich et al., 2021) was deployed to detect PAN, HONO and HNO$_3$. The I-CIMS was coupled to the SCHARK via $\approx$ 2m of ¼ inch PFA tubing heated to 40 °C. The flow rate through the PFA-tubing was ~2.1 SLM. Iodide anions were generated by passing 4 sccm of 400 ppmv methyl iodide (CH$_3$I in N$_2$) diluted in 750 sccm N$_2$ (Westfalen, 5.0) through a 370 MBq polonium (^{210}Po) source. PAN was thermally dissociated in an heated inlet (PFA tube at 170°C, residence time of 40 ms) to peroxy acetyl radicals which are detected as acetate ions CH$_3$CO$_2^-$ (m/z 59) after reaction with I$^-$ (Phillips et al., 2013). Calibration was performed using a photochemical PAN source (Warneck and Zerbach, 1992). HNO$_3$ was detected as the I$^-$(HNO$_3$) cluster ion at m/z 190 and calibrated using an HNO$_3$ permeation source characterised by optical absorption. HONO was detected as NO$_2^-$ (m/z 46) using acetate anions (Veres et al., 2008) generated by adding a high concentration of PAN to the TD-inlet.
We refer to this in the main text in L258-260:
In order to identify the trace-gas(es) responsible for the signals observed in the system without isoprene, an Iodide-Chemical-Ionization Mass Spectrometer (I-CIMS (Eger et al., 2019)) described in the Supplement (S8) was coupled to the experiment.

Line 267. How was the mixing ratio of 22 ppbv HNO3 determined?
The HNO$_3$ mixing ratio was calculated from the permeation rate and flow rates. We added the following text to L267:
In these experiments, 22 ppbv HNO$_3$ with 780 pptv NO$_2$ impurity in dry synthetic air was delivered to the TDIs along with 350 ppbv O$_3$. The HNO$_3$ mixing ratio was derived using a known permeation rate (Friedrich et al. 2021) and dilution factor.

Line 279 "by the scavenging of O-atoms". While this is plausible explanation, please note the speculative nature of this statement. Rather than scavenging O atoms, the surface could act to catalyze 2O->O2, for instance.
We agree and modify this sentence in L279:
In TDI-1 this is prevented by the removal of O-atoms by the glass beads (e.g. via scavenging or surface-catalysed recombination to O$_2$).

line 288. "H2O drives HNO3 from the surface and thus protects it from surface reactions". How much water would you expect to be sorbed to surfaces in an inlet heated well above the boiling point of water?
At high temperatures, the physi-adsorption of water is of course greatly reduced but not zero. One must bear in mind, that the concentration of H$_2$O relative to HNO$_3$ is very large and competitive adsorption will play a role in determining the surface adsorption (and thus further reactions) of HNO$_3$.

line 350-351. The instrument must have sampled a very large concentration of nitric acid for a long time to produce such a large artifact.
Correct, but especially the example shown in Fig. S4 was measured before we were aware of that problem and after the unheated TDI sampled air from the SCHARK containing residual HNO$_3$ and ISOP-NIT for several hours. Given the fact that keeping the TDI below 400 K for ca. 30 minutes while sampling ca. 2.8 ppbv ISOP-NIT (and probably HNO$_3$) is sufficient to create a peak signal of ca. 10 ppbv when heating back to 703 K (see Fig. S5), this appears plausible.

line 400. Replace Torr with SI units, please.
Correction made, instead of Torr we now use hPa. The same was done in L138 and L176.

line 423. Please move the experimental details to the experimental section.
We are aware of the fact that it is unconventional to provide experimental details in the results section. But since this is a special modification of the setup that is only relevant in this paragraph, we are convinced that it is easier to follow the manuscript, if the details are kept at this place.

References

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