We thank both reviewers for their constructive criticisms.

Response to Reviewer #1

It is not obvious that changes in inlet residence time and the calculated impact warrants publication.

We have revised the introduction to stress the aspects of the paper that are new and made changes throughout the paper to clarify the unique contributions in this manuscript.

No testing of the improved performance (e.g., using laboratory $CH_3O_2NO_2$ *or* HO_2NO_2 *samples) was performed and indeed it appears that the fundamental quantity (the temperature of the thermally dissociating gas) was not measured but only assumed.*

In our opinion, there is sufficient knowledge from prior laboratory experiments to outline an experimental procedure for field observations (e.g., Day et al., 2002; Wooldridge et al., 2010). Direct field measurements are the crucial test of the efficacy of that procedure. While we are not able to synthesize the target molecules in our laboratory, we discuss in the manuscript atmospheric measurements we utilized to test the measurement strategy. These tests would be necessary even if we were able to synthesize the target molecules in our laboratory.

I assume that the authors will publish their $CH_3O_2NO_2$ *dataset fully elsewhere and propose that the limited useful information in this document would be suitable as supplementary information to that paper.*

As of today, we have no intention of publishing the $CH_3O_2NO_2$ data set elsewhere. The data has been publically available for 1 year for DC-3 and recently the SEAC4RS data was made publically available. In our opinion, the methods described here for characterizing $CH_3O_2NO_2$ and for showing how to measure NO_2 with minimal $CH_3O_2NO_2$ interference or corrected for $CH_3O_2NO_2$ interference described in this text are useful contributions to the literature independent of an analysis of the scientific implications of the $CH_3O_2NO_2$ observations.

P 9455 L 20: The temperature of the UT is not circa 225 K as implied here, but can deviate significantly from this. Better to give a range of temperatures for the UT but indicate that the lifetimes of HO_2NO_2 *and* $CH_3O_2NO_2$ *are given at 225 K, as an example.*

We thank the reviewer and have made the appropriate changes to the text.

P 9455 L 25: The text here and on the next page makes little sense. Changes in NO_x, HNO_3, and O_3 resulting from including $CH_3O_2NO_2$ in the model are somehow listed twice.

We revised the text to clarify the point we were making.

P 9456 L 11: "It should be presumed that most other NO_2 instruments suffer from the same interferences". Why not indicate here why we should presume this. What are the instruments we are discussing and what are the associated inlet temperatures and residence times?

We modified the sentence to read:

"At room temperature, $CH_3O_2NO_2$'s lifetime is shorter than a second (Fig. 1). If the air sample is brought into a warm aircraft prior to detection, this very short lifetime results in substantial decomposition for residence times longer than even 0.1 s (Fig. 2). As a result of the decomposition of $CH_3O_2NO_2$, there is also a positive interference to NO_2 measurements with residence times at warm temperatures longer than 0.1 s. For NO_2 measurements, the interference was quantified to be as much as 43% during a study over Canada in springtime (Browne et al., 2011)."

P 9456 L 20: The authors state that "… these measurement are the first to isolate $CH_3O_2NO_2$ directly." In fact they do not isolate $CH_3O_2NO_2$ as HO_2NO_2 is (partially) co-detected as discussed later.

We have changed the sentence to read:

"These measurements are the first in-situ measurements providing specific information about atmospheric $CH_3O_2NO_2$.."

P 9459 L1-28. The text is unwieldy and largely a qualitative read-through of the data listed in Table 1. This can be shortened considerably.

We changed the lines to shorten the text.

P 9457 L 22 and in other places in the text. As I understand, the inlet temperature given (60°C) is the temperature of the outside wall of a quartz tube. It is not the gas temperature, which was not determined. This needs to be made clear as the subsequent calculations all assume that the thermally dissociating gas ($CH_3O_2NO_2$ or HO_2NO_2) is at the temperature of the walls. In this *context, how was the "uncertainty" in the oven temperature (P9460, L25) derived? Why did the authors do no laboratory tests to test the losses of $CH_3O_2NO_2$ and HO_2NO_2?*

We have added the following text to address this concern:

"The lower maximum temperatures of the $CH_3O_2NO_2$ and sum of peroxy nitrates (ΣPNs) heaters compared to the sum of alkyl and multifunctional nitrates (ΣANs) heaters (Fig. 5) allow for a simpler construction, as described in Wooldridge et al. (2010). Instead of bare nichrome wire, commercial woven fiberglass insulated heating cables are used, and thermocouples are fastened directly to the quartz tubes. The very small amount of heat required to bring the sample streams to 60°C (~ 1 W for $CH_3O_2NO_2$, as calculated from the air heat capacity and mass flow rates) means that neither the maximum heater power (50 W across the 0.175 m heated length for $CH_3O_2NO_2$ dissociation) or the quartz tube thermal resistance are limiting factors that would cause the thermocouple measurement to differ significantly from the internal gas temperature. Additionally, using the constant wall temperature approximation (e.g., Kliner et al., 1997; reference therein), we calculate thermal equilibration lengths of 0.01 – 0.02 m for $CH_3O_2NO_2$, which are short compared to the overall heated lengths (0.175 m)."

We do not have the equipment in our laboratory to synthesize and purify $CH_3O_2NO_2$ and HO_2NO_2.

Instead, we took advantage of the thermal stability of $CH_3O_2NO_2$ to indicate that at high temperatures, the $CH_3O_2NO_2$ channel is measuring similar mixing ratios as the NO_2 channel, but at colder temperatures, the $CH_3O_2NO_2$ channel is measuring higher values than the NO_2 channel. Also, we emphasize that Fig. 8 (scatter plot of inferred versus measured $CH_3O_2NO_2$) indicates that the temperature selected is fully thermally decomposing $CH_3O_2NO_2$ with minimal thermal decomposition of HO_2NO_2.

P9462, L 9. Why do the authors believe that the factor two in the PSS calculations of HO_2NO_2 is a transferable quantity? What does "we observe a similar" result mean?

Since this discussion creates confusion and the explanation is beyond the scope of this paper, we have removed discussion of the difference between model and observed HO_2NO_2.

P9463, L23. Why pick out acetaldehyde as an example. Where is acetaldehyde an important source of $CH_3O_2NO_2$?

We have changed the text to read:

"Even though the temperatures in the lower stratosphere are low enough for the $CH_3O_2NO_2$ lifetime to be greater than 10 h, the observations indicate that the lower stratosphere has lower mixing ratios of the precursors of CH_3O_2. These include the peroxy acyl radical from acetaldehyde, which reacts with NO to produce CH_3O_2 (e.g., Tyndall et al., 2001), and

CH_3COCH_3, which can photolyze to produce CH_3O_2 (e.g., Folkins and Chatfield, 2000; Jaeglé et al, 2001; Neumaier et al., 2014).”

P9464. The discussion is a half-hearted analysis of the $CH_3O_2NO_2$ data-set. It’s not obvious why this is appropriate in an AMT paper.

We revised this text, our purpose was not to present an analysis of the role of $CH_3O_2NO_2$ but rather to indicate that the measurement method is providing scientifically useful observations.

References

Folkins, I. and Chatfield, R.: Impact of acetone on ozone production and OH in the upper troposphere at high NO_x, J. Geophys. Res., 105, 11585–11599, doi:10.1029/2000JD900067, 2000.

Jaeglé, L., Jacob, D. J., Brune, W. H., and Wennberg, P. O.: Chemistry of HO_x radicals in the upper troposphere, Atmos. Environ., 35, 469–489, doi:10.1016/S1352-2310(00)00376-9, 2001.

Kliner, D. A. V., Daube, B. C., Burley, J. D., and Wofsy, S. C.: Laboratory investigation of the catalytic reduction technique for measurement of atmospheric NO_y, J. Geophys. Res., 102, 10759–10776, doi:10.1029/96JD03816, 1997.

Neumaier, M., Ruhnke, R., Kirner, O., Ziereis, H., Stratmann, G., Brenninkmeijer, C. A. M., and Zahn, A: Impact of acetone (photo)oxidation on HO_x production in the UT/LMS based on CARIBIC passenger aircraft observations and EMAC simulations, Geosphy. Lett., 41, 3289–3297, doi:10.1002/2014GL059480, 2014.

Tyndall, G. S., Cox, R. A., Granier, C., Lesclaux, R., Moortgat, G. K., Pilling, M. J., Ravishankara, A. R., and Wallington, T. J.: Atmospheric chemistry of small organic peroxy radicals, J. Geophys. Res., 106, 12157–12182, 2001.

Response to Reviewer #2

General comments

1. It seems like more could have been done to validate the experimental technique. Have there been any laboratory validation experiments? How about in-field comparisons of HO_2NO_2 *measured by TD-LIF and CIMS? Why are only the CIMS data shown?*

We do not have the ability to create known quantities of HO_2NO_2 or $CH_3O_2NO_2$. To our knowledge, few laboratories have such ability. Many upper tropospheric NO_2 measurements have been made without laboratory tests for interferences of HO_2NO_2 or $CH_3O_2NO_2$. We agree such measurements would be useful and hope they will emerge in the future.

We showed the CIMS HO_2NO_2 since only CIMS measured HO_2NO_2 while we measured the sum of HO_2NO_2 and PAN like species.

2. What's lacking in this paper is a prediction of $CH_3O_2NO_2$ *and a comparison of predicted with observed values.*

We have included a figure and discussion comparing modeled to measured $CH_3O_2NO_2$. We hope that the other reviewer does not find that this figure goes too far into analysis of the data for it to be appropriate for AMT.

3. The paper could have been more interesting by showing more of the in-flight data.

We have added another figure with in-flight data.

Specific comments

Page 9454, line 4. In the abstract, it is claimed that these are the first measurements of methyl peroxy nitrate. Considering that this group has published on HO_2NO_2 *and* $CH_3O_2NO_2$ *in the past, these are hardly the first measurements of this compound, but perhaps the first selective measurements – certainly not specific, as contributions from* HO_2NO_2 *still not to be subtracted.*

The prior publication from this group on HO_2NO_2 and $CH_3O_2NO_2$ were indirect measurements of these species. We changed the line to read:

"These measurements are the first in-situ measurements providing specific information about atmospheric $CH_3O_2NO_2$."

Line 9 "have lower thermal stability" – can you the authors be more quantitative here? Perhaps give relative bond dissociation energies?

We changed the line to read:

"The emphasis on low temperatures results from non-acyl peroxy nitrates, such as $CH_3O_2NO_2$ and pernitric acid (HO_2NO_2), having lower thermal stability and shorter lifetimes than acyl peroxy nitrates, such as peroxy acetyl nitrate (PAN) and peroxy proionyl nitrate (PPN) (~100 kJ/mol for non-acyl peroxy nitrates versus ~120 kJ/mol for acyl peroxy nitrates)."

Pg 9455 lines 5 – 6. It is claimed that ethyl and acetone peroxy nitrate are not abundant enough to interfere, and papers are cited (as if they were fact) in which that assumption was made by the same group. I don't think that the authors are wrong here, but please don't give the wrong impression that this is anything other than an assumption.

We removed discussion of this point in the revised introduction.

Pg 9455, line 15/16 (R1 and R2) and Table 2 (pg 9470) The double-headed arrow is used by chemists to denote resonance structure – please replace with the appropriate symbol for equilibrium.

We replaced all the ↔ with ⇌.

Pg 9455, lines 20 – 23. The authors state lifetimes, but it is not clear on what basis these were calculated – based on rates by Sander et al., or are these values derived from observations perhaps.

We have changed the caption to state how the lifetime was calculated (see below).

Pg. 9456, line 14 and pg. 9460, lines 4 and 14. For a chemist, "X" would imply a halide – it would be more appropriate to use RO_2NO_2 to refer to non-acyl peroxy nitrates.

We keep the X for consistency with the terminology introduced by Browne et al. (2011) and used in the subsequent publication by Henderson et al., 2012. The X is not used to refer to non-acyl peroxy nitrates but rather to the measurement of NO_2 with some positive interference due to the thermal decomposition of non-acyl peroxy nitrates (Browne et al., 2011). We think that readers will recognize the definition we are using.

Line 20 "… to isolate $CH_3O_2NO_2$ directly." Since $CH_3O_2NO_2$ is measured indirectly, consider rephrasing to "… to isolate the $CH_3O_2NO_2$ signal."

We changed the sentence to reflect the suggestion.

Pg 9457, lines 16 – pg 9458 line 10. Can the authors comment on the possibility and extent of recombination reactions (e.g., of $CH_3O_2 + NO_2$) and of the possibility and extent of either HO_2 or CH_3O_2 oxidizing NO and creating a "fake" signal?

We will add the following text to clarify this issue.

"The transmission efficiency depends on recombination reactions and oxidation of NO. Day et al. (2002) and Wooldridge et al. (2010) showed these to be small effects (~5 – 10%) at NO mixing ratios less than 1 ppbv and pressures in the inlet region less than 400 hPa (ambient pressure). Assuming mixing ratios of 100 pptv for $CH_3O_2NO_2$ and HO_2NO_2, 200 pptv for NO_2 and 100 – 5000 pptv NO, we calculate a positive interference to $CH_3O_2NO_2$ measurements ranging from ~8 – 26% from the oxidation of NO to NO_2. The typical NO mixing ratios at the temperatures where $CH_3O_2NO_2$ is stable range from ~50 – 400 pptv (25th – 75th percentile), and for this range, we calculate a positive interference of less than 10%."

Pg 9458, line 11. "Interference free NO_2." This title is misleading as there always is a water interference with this technique (see pg 9457 – lines 13 – 15).

We changed the title to "NO_2 measurements free of non-acyl peroxy nitrate interference".

Pg 9461 line 6. I didn't like that the uncertainty as described as a single number (40%). Shouldn't it be a function of HO_2NO_2, NO, and NO_2? In other words, the uncertainty could be much higher than 40% if there was more HO_2NO_2 that needed to be subtracted.

We will change pg 9461 lines 4 – 7 to read:

"To summarize, the largest source of uncertainty in the $CH_3O_2NO_2$ measurement is the uncertainty of the thermal decomposition rate for $CH_3O_2NO_2$ (~30%). Other effects, including recombination reactions and the thermal decomposition of HO_2NO_2, are each typically less than 10%. Combining these uncertainties we estimate a total uncertainty of ±40% for the $CH_3O_2NO_2$ measurements. We note that the sum of the NO_2 and $CH_3O_2NO_2$ measurement ($CH_3O_2NO_{2,CHANNEL}$) is more accurate (~5−10%) than the separate quantities."

Pg 9462, line 3 (equation 3) and lines 9 – 10. "We observe a similar result; therefore, we divide the calculations by 2 to reflect that result." This is interesting. Even with this arbitrary fudging, the predicted values are still quite a bit too high, if I interpret Figure 6 correctly. Earlier (pg 9455, line 20) it is stated that the lifetime of HO_2NO_2 *is typically 7 hours. Under these conditions, it may take more than a day to get a photostationary state. The assumption going into the pss (i.e., equation (3)) may be invalid if the* HO_2NO_2 *lifetime really is long. Couldn't the* HO_2NO_2 *concentrations not have been simulated using a simple box model? How about attempting to predict* $CH_3O_2NO_2$ *(and comparing to measurements)?*

Since this discussion creates confusion and explanation is beyond the scope of this paper, we have removed discussion of these calculations. We have included a figure and discussion comparing calculated and measured $CH_3O_2NO_2$.

line 11 (the time 7.5 and 8×10^4 *s". Please convert to more convectional units of time (hours, minutes). UTC is great, but it would also be helpful to know what time zone you were in (and what local time it was then).*

We changed the time from s to UTC (hr). We were constantly changing time zones (and hence solar zenith angles) while flying, so we will give approximate local times.

Pg 9472. Figure 1. Please state in the caption how these lifetimes were calculated.

We changed the caption to read:

"Calculated mean total lifetime profile of $CH_3O_2NO_2$ (blue) and HO_2NO_2 (green) for typical conditions observed during DC-3 in the daytime. The total lifetime is calculated using observed OH, photolysis rates, and temperatures along with the rate constants listed in Table 2. The black line is marks the region where the non-acyl peroxy nitrates have a lifetime longer than 1 hour."

Pg. 9477. Why is the predicted data missing after 8×10^4 *s? In the caption of Figure 6, please remove the hyphen between ionization and mass.*

We have changed the caption to read:

"Five minute averaged time series of **(a)** uncorrected (black) and corrected (magenta) $CH_3O_2NO_2$ for HO_2NO_2 thermal decomposition, **(b)** HO_2NO_2, and **(c)** pressure altitude (blue) and temperature (green) from a flight on 30 May 2012 during DC-3. Local sunset is approximately 00:00 UTC."

Pg 9479. Please state the r value of the fit.

We included in the caption:

“The R^2 of the fit is 0.3.”