

Response to reviewer #1's comments

Reviewer comments are in **bold**. Author responses are in plain text. Excerpts from the manuscript are in *italics*. Modifications to the manuscript are in *blue italics*. Page and line numbers in the responses correspond to those in the original AMTD paper.

The authors are describing experimental findings from an online method for the detection of thermalized Criegee intermediates (CI) and RO₂ radicals in different laboratory setups. CIs have been observed via HFA titration or DMPO derivatization and RO₂ radicals via DMPO or TEMPO derivatization. Analysis was carried out by means of a PTR3 mass spectrometer running in the H₃O⁺ or NH₄⁺ mode. CI detection via HFA adducts was successful in the case of the ozonolysis of TME, isoprene, pentene and hexene, but not for the expected CIs arising from the ozonolysis of selected terpenes. Also the simplest CI, CH₂OO, was not measurable. Examples for RO₂ measurements are given from the ozonolysis (incl. OH reaction?) of TME and alpha-pinene. The stated detection limit for CIs is about 10⁷ molecules/cc and that for RO₂ about 10⁸ molecules/cc for 30 s integration time. The topic of this paper is well suited for AMT. Some clarifications are needed before publication can be recommended.

We would like to thank the reviewer for the positive reception of our work and constructive comments that helped us to improve our manuscript. Below we provide our replies to the reviewer's comments. Page and line numbers in the responses correspond to those in the AMTD paper.

- 1. Line 53: Atmospheric RO₂ radical concentrations in the order of 10⁸ molecules/cc are not generally valid. It stands mainly for CH₃O₂, concentration levels of other RO₂ radicals can be much lower.**

We modify the following sentence by specifying ambient concentrations of RO₂ species (P2 L52):

Highly sensitive detection systems are required to determine the minute concentrations of these species, which are typically on the order of 10⁸ molecule cm⁻³ for organic peroxy radicals (Fuchs et al., 2008) and are expected to be less than 10⁵ molecule cm⁻³ for SCIs (Novelli et al., 2017). Concentrations of the smallest organic peroxy radicals, CH₃O₂, are typically on the order of 10⁸ molecule cm⁻³ while concentrations of other RO₂ species can be much lower (Fuchs et al., 2008). As for SCIs, their concentrations are expected to be less than 10⁵ molecule cm⁻³ (Novelli et al., 2017).

- 2. Line 104: Please provide a table with the initial reactant concentrations and the calculated amount of reacted olefin for a better understanding what has been done.**

We include the following table containing the initial reactant concentrations and the calculated amount of reacted olefin in the SI:

Table S2: Descriptions of ozonolysis experiments with HFA

<i>Olefin</i>	<i>Initial olefin concentration, molecule cm⁻³</i>	<i>O₃ concentration, molecule cm⁻³</i>	<i>HFA concentration, molecule cm⁻³</i>	<i>Calculated amount of reacted olefin, %</i>
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TME	$1.85 \cdot 10^{12}$	$1.67 \cdot 10^{13}$	$6.09 \cdot 10^{15}$	17%
isoprene	$1.23 \cdot 10^{13}$	$3.20 \cdot 10^{14}$	$5.35 \cdot 10^{15}$	6%
pentene	$4.18 \cdot 10^{13}$	$6.15 \cdot 10^{13}$	$5.35 \cdot 10^{15}$	14%
hexene	$2.21 \cdot 10^{13}$	$2.95 \cdot 10^{14}$	$5.35 \cdot 10^{15}$	50%
α -pinene	$2.70 \cdot 10^{12}$	$3.20 \cdot 10^{14}$	$5.35 \cdot 10^{15}$	37%
limonene	$2.10 \cdot 10^{12}$	$3.45 \cdot 10^{14}$	$5.35 \cdot 10^{15}$	67%

3. Line 143: Also here, please state the initial reactant conditions. What was the residence time in the respective flow tubes? If I understand it right, in the first flow tube the O₃(OH?) + TME/alpha-pinene reaction was running without OH scavenger and the second flow tube served for product derivatization by DMPO (but TME/alpha-pinene conversion was still running)? Please provide a more precise insight what's going on in the different parts of this flow-through experiment.

We add the following discussion on the experimental setup used during the ozonolysis experiments with spin trap DMPO (P5 L146):

Experimental setup consisted of two identical ~2.1L flow reactors. The parent hydrocarbon was mixed with ozone in the first flow tube reactor with a residence time of ~28s. Similar to the previous ozonolysis experiments described in Sect. 2.1, the parent olefin was vaporized from a flask filled with pure substance by passing zero air regulated by a mass flow controller, and ozone was generated using a low-pressure mercury ultraviolet lamp. while the spin trap DMPO (C₆H₁₁NO) was introduced in the second flow tube using an LCU. We used an LCU to introduce the spin trap DMPO in the second flow reactor with a residence time of ~23s. A known amount (up to 10 μ L min⁻¹) of the DMPO solution was evaporated into a humidified gas stream of synthetic air (5.4-7 SLPM), resulting in the gas-phase DMPO concentration of up to 1.1×10^{13} molecule cm⁻³. The second flow reactor served for derivatization of SCIs and RO₂ species by DMPO while the parent hydrocarbon was still reacting with ozone. Hence, we conducted integrated production measurements of SCIs and RO₂ species formed in both flow reactors. The PTR3 was used to detect spin trap adducts with SCIs and RO₂ species SCI-DMPO and RO₂-DMPO adducts, while ozone levels were observed using an ozone monitor (2B Technologies).

In addition, we include the following table containing the initial reactant concentrations and the calculated amount of reacted olefin in the SI:

Table S3: Descriptions of ozonolysis experiments with DMPO

Olefin	Initial olefin concentration, molecule cm ⁻³	O ₃ concentration, molecule cm ⁻³	DMPO concentration, molecule cm ⁻³	Calculated amount of reacted olefin, %
TME	$3.69 \cdot 10^{11}$	$7.87 \cdot 10^{12}$	$2.01 \cdot 10^{12}$	43%
α -pinene	$4.92 \cdot 10^{11}$	$1.03 \cdot 10^{13}$	$1.10 \cdot 10^{13}$	9%

4. Line 186: The Donahue group, ref: 10.1021/jp108773d, used $k_{(\text{CH}_3)_2\text{COO}+\text{HFA}} = 2 \times 10^{-13} \text{ cc/s}$, about 2 orders of magnitude lower as the rate coefficient used in this work. Is the HFA concentration still high enough for complete conversion of $(\text{CH}_3)_2\text{COO}$ with HFA?

Since the proton affinity of HFA is lower than that of water, we were able to introduce significant amounts of HFA (see Table S2 above) to make sure that HFA remains the major chemical loss even if $k_{(\text{CH}_3)_2\text{COO}+\text{HFA}} = 2 \times 10^{-13} \text{ molecule cm}^{-3} \text{ s}^{-1}$. We update Fig S3 in the SI:

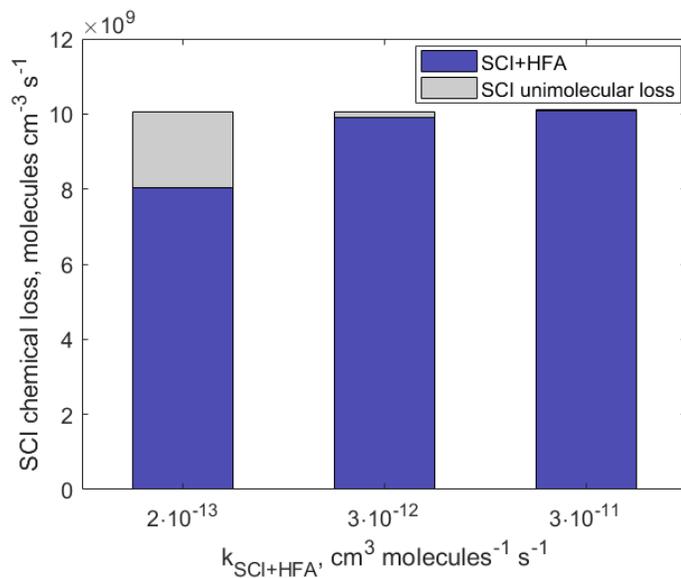


Figure S3: Chemical losses of stabilized Criegee intermediates $(\text{CH}_3)_2\text{COO}$ calculated assuming different $k_{\text{SCI}+\text{HFA}}$ reaction rates under experimental conditions. $k_{\text{SCI}+\text{HFA}} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ corresponds to the rate constant for $\text{CH}_2\text{OO} + \text{HFA}$ reaction (Taatzjes et al., 2012). Previous studies used lower rate constant ($2 \times 10^{-13} \text{ molecule cm}^{-3} \text{ s}^{-1}$; Drozd et al., 2011). Even at lower values of the reaction rate the major chemical loss pathway for SCI is the reaction with HFA.

We also add the reference to the work by the Donahue group in the manuscript (P6 L187):

It has been suggested that the reaction between HFA and acetone oxide may be slower compared to the CH_2OO one (Murray et al., 1965; Taatzjes et al., 2012) while $k_{(\text{CH}_3)_2\text{COO}+\text{HFA}} = 2 \times 10^{-13} \text{ molecule cm}^{-3} \text{ s}^{-1}$ was used in the previous studies (Drozd et al., 2011).

5. Line 197: How good is the agreement model vs. measurement in the case of the ozonolysis of isoprene, pentene and hexene?

In the case of the ozonolysis of isoprene, pentene and hexene, our measurements of SCI·HFA are one to two orders of magnitude lower than the model prediction. There are several factors that can contribute to this discrepancy:

1. Yields of SCIs for larger intermediates might be off. MCM assumes the same yield of 0.18 for CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHOO}$, however, measured yields of these intermediates vary by up to a factor of 2 (Newland et al., 2015 and references therein). In

addition, some studies suggested that yields of larger SCIs (e.g., C₄-SCI) are significantly smaller than that of CH₂OO (Nguyen et al., 2016).

2. Unimolecular decomposition of SCI is not taken into account in the model. MCM includes only bimolecular loss reactions for CH₃CHOO, CH₃CH₂CHOO and CH₃CH₂CH₂CHOO, while some studies suggest that SCI unimolecular rates increase with size and become more important (Nguyen et al., 2016; Newland et al., 2015).
3. The reaction rate coefficient between larger SCI and the derivatization agent HFA is unknown. As the reviewer pointed out earlier, the reaction rate coefficient is expected to be lower for larger SCIs, but it has not been measured directly. While we introduced significant amounts of HFA in the experimental system to ensure that the reaction with HFA remains the major chemical loss for SCIs, we cannot be certain that all SCIs were scavenged by HFA.

Based on these factors and associated uncertainties in both the model and measurements, we think that presenting the model vs. measurement agreement for isoprene, pentene, and hexene falls beyond the scope of this study.

6. **Line 204: What is the detection limit of OH radicals via the TEMPO derivatization as a result of this work? Giorio et al., ref:10.1021/jacs.6b10981, were not able to follow OH production from alpha-pinene ozonolysis using a similar technique. Is it really possible to measure steady-state OH in a reaction system by means of this technique?**

We estimate the detection limit of OH radicals via the TEMPO derivatization for our setup to be $\sim 6 \times 10^6$ molecule cm⁻³. This limit of detection is calculated for a 1 s integration time of TEMPO·OH signal as three standard deviations of measured background divided by derived sensitivity for TEMPO. The purpose of TEMPO derivatization experiments was to demonstrate that chemical derivatization agents, including spin traps, are highly reactive towards atmospheric radicals and reactive intermediates rather than to fully describe this method to detect OH radicals. As we state in the manuscript (P7 L219), further tests are required to compare the measurement capability of this method with that of a well-established technique, such as LIF. Whether steady-state OH concentration can be measured will depend on the experimental setup and what averaging time is acceptable. For example, with 10 min averaging the detection limit can be reduced to 2.5×10^5 molecule cm⁻³, which is in a useful range. Furthermore, other CIMS instruments have achieved lower detection limits. Thus, we believe detection of OH is feasible, depending on conditions and instrumentation. While we agree with the reviewer that it would be interesting to check if it would be possible to observe OH from α -pinene ozonolysis, we think that conducting such experiments lies beyond the scope of this manuscript.

7. **Line 222: I think these experiments have been done in the double flow-tube setup, right? So, you should see the resulting RO₂ radicals from ozonolysis as well as those from the OH reaction if no OH scavenger is used. That means in the case of TME also the primarily formed HO-C₆H₁₂O₂ radicals should be visible in addition to acetylperoxy radicals from the ozone reaction? And in the case of alpha-pinene, HO-C₁₀H₁₆O₂ radicals (and subsequent autoxidation products) must be there along with the ozonolysis-derived RO₂s. Please comment!**

We observed formation of RO₂ species formed via OH-oxidation of TME. We include the following discussion (P8 L239) and edit Fig. 6 by adding the corresponding tracer to it:

OH radicals, formed via decomposition of SCI, can in turn react with TME and lead to formation of another RO₂ species OH-C₆H₁₂OO·. This radical was detected as the C₆H₁₃O₃·DMPO adduct (C₁₂H₂₄NO₄, m/z 264.205; Fig. 6).

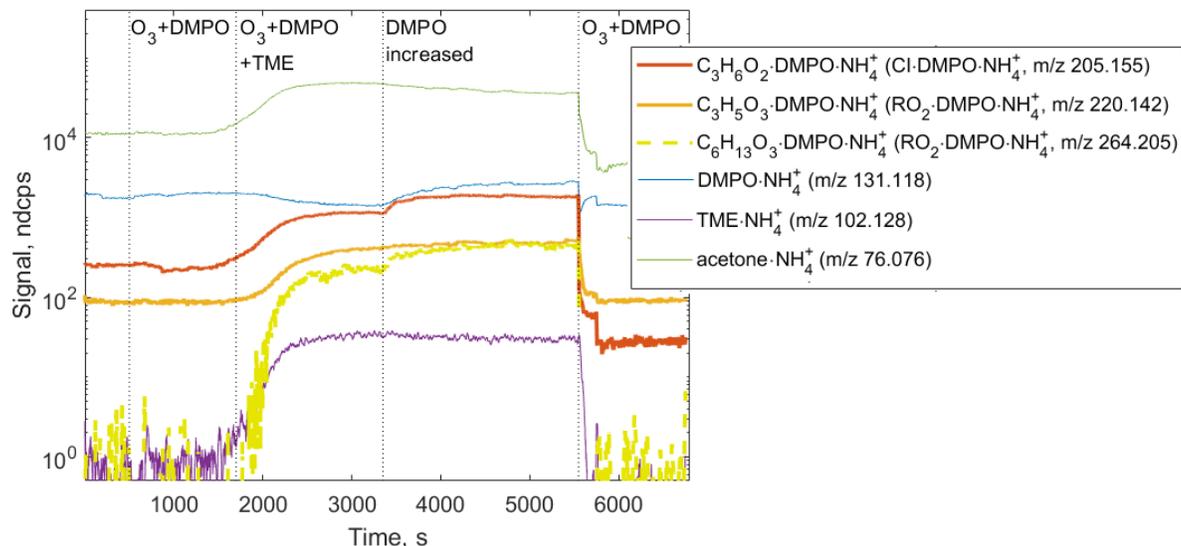


Figure 6: Ion tracers observed by NH₄⁺ CIMS in a TME ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are [TME] = 3.69 × 10¹¹; [O₃] = 7.87 × 10¹²; [DMPO] = 2.01 × 10¹² molecule cm⁻³.

In addition, we also observed formation of HO-C₁₀H₁₆O₂ species and subsequent autooxidation products in the case of α -pinene. We include the following discussion (P9 L261) and edit Figs. S10 and S11:

OH radicals, formed via decomposition of SCI, can in turn react with α -pinene and lead to formation of OH-derived RO₂ species C₁₀H₁₇O₃ and subsequent autoxidation RO₂ species C₁₀H₁₇O₅ (Berndt et al., 2016). These radicals were detected as the RO₂·DMPO adducts (Figs. S10 and S11).

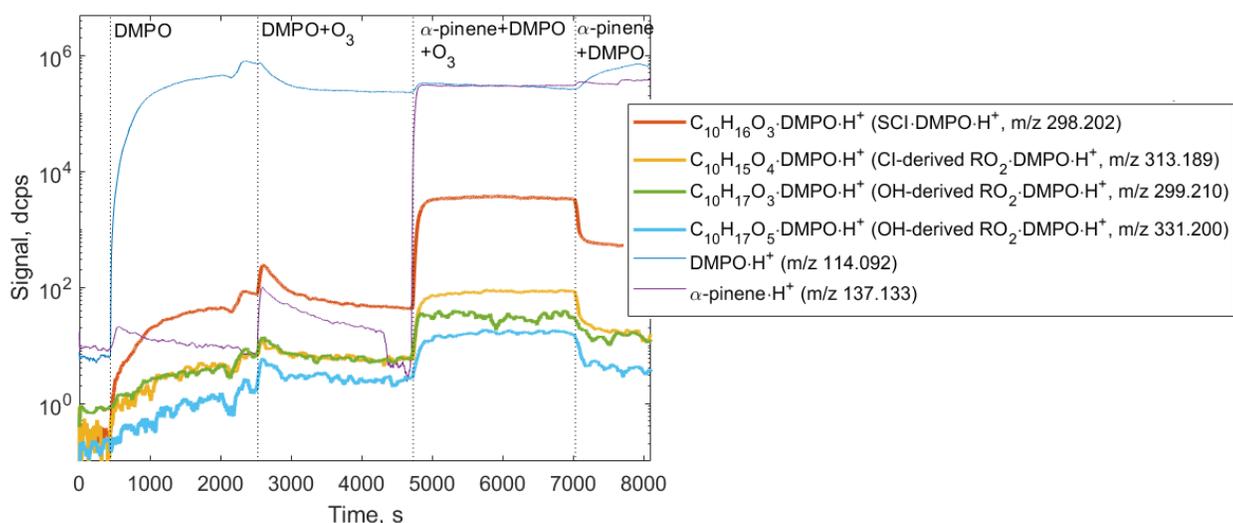


Figure S10: Ion tracers observed by H_3O^+ CIMS in an α -pinene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\alpha\text{-pinene}] = 4.92 \times 10^{11}$; $[O_3] = 1.03 \times 10^{13}$; $[DMPO] = 1.10 \times 10^{13}$ molecule cm^{-3} .

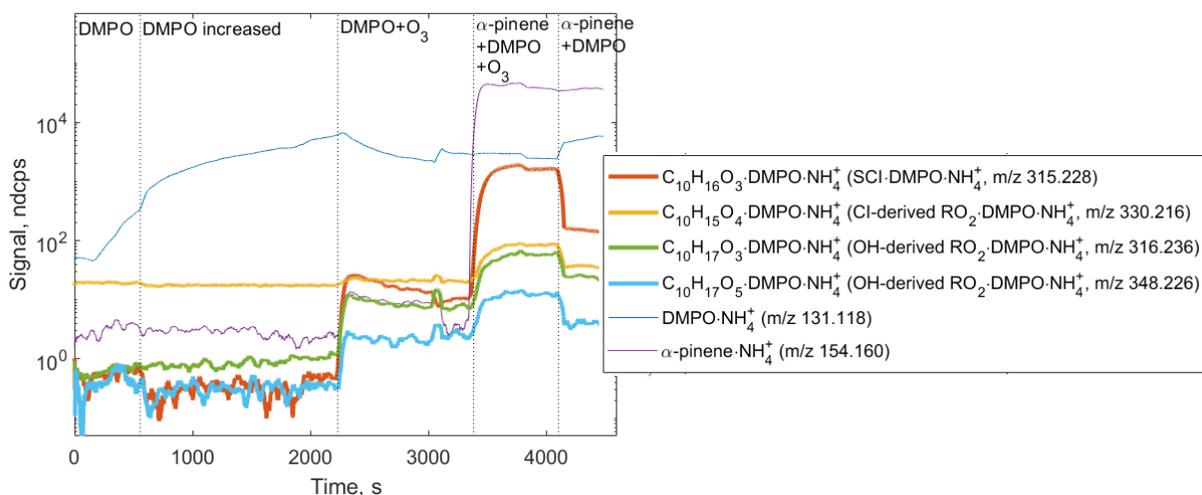


Figure S11: Ion tracers observed by NH_4^+ CIMS in an α -pinene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\alpha\text{-pinene}] = 4.92 \times 10^{11}$; $[O_3] = 1.03 \times 10^{13}$; $[DMPO] = 1.10 \times 10^{13}$ molecule cm^{-3} .

8. Another point: Hansel et al., ref: [10.1016/j.atmosenv.2018.04.023](https://doi.org/10.1016/j.atmosenv.2018.04.023), are stating a detection limit of 2×10^5 molecules/cc for RO_2 radicals and closed shell products from cyclohexene ozonolysis using a similar (or same) mass spec with NH_4^+ ionization. That means the authors should be able to monitor the RO_2 radicals directly at the outflow w/o derivatization? That could be helpful for the assessment of the derivatization procedure.

We agree with the reviewer that it would be interesting to conduct simultaneous measurements of RO_2 species with and without using derivatization agents, however, our setup was not designed for this type of experiments. In addition, there are several disadvantages associated with direct

measurements of RO₂ species: (1) potential interferences from secondary chemistry, i.e., additional sources or radical production and destruction as well as their cycling, have to be taken into account; (2) losses of radicals on the walls in the experimental setup and inside the instrument have to be considered; and (3) potential interferences with isotopes of closed-shell molecules can impede quantification of detected RO₂ species. For example, an isotope of pinonic acid (*m/z* 203.148 in NH₄⁺ CIMS) strongly overlaps with OH-derived RO₂ species formed via oxidation of α -pinene (*m/z* 203.152 in NH₄⁺ CIMS).

- 9. Line 259 and fig.8: Higher oxidized RO₂ radicals arising from pure autoxidation steps show a mass difference of 32 mass units due to step-by-step insertion of molecular oxygen. A mass difference of 16 mass units points to efficient bimolecular RO₂ steps altering the autoxidation-governed RO₂ distribution. So, as already said, it would be fine to have the complete reaction conditions to get an idea how important RO₂ + RO₂ could be.**

The reviewer raises an interesting point. We agree that having a more complete understanding of the importance of RO₂ self-reactions could be beneficial for this study. However, to the best of our knowledge, kinetics of autoxidation and self-reactions is well studied for smaller RO₂ species only. Hence, we believe that determining the relative importance of chemical loss channels for RO₂ species lies beyond the scope of this study.

References:

Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjær, R.V., Kjaergaard, H.G., Stratmann, F., Herrmann, H., Sipilä, M., Kulmala, M., and Ehn, M.: Hydroxyl radical-induced formation of highly oxidized organic compounds, *Nature Communications*, 7, 13677, DOI: 10.1038/ncomms13677, 2016.

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