Response to reviewer #2'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.

This study presents the development of an online method for measurements of SCIs and RO₂ in laboratory experiments using chemical derivatization and spin trapping techniques combined with H₃O⁺ and NH₄⁺ chemical ionization mass spectrometry. Application of this method is demonstrated using laboratory ozonolysis experiments of multiple hydrocarbons including TME, isoprene, pentene, hexene, alpha-pinene and limonene. The detection limits of spin trap and chemical derivatization agent adducts are estimated to be $1.4 \cdot 10^7$ molecule cm⁻³ for SCIs and $1.6 \cdot 10^8$ molecule cm⁻³ for RO₂ for 30 s integration time for the instrumentation used in this study. This manuscript is well written and within the scope of the journal. I recommend this manuscript to be published in AMT after the following issues be addressed.

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. **Page 6, Line 166-167: Is there any evidence for using HFA with SCIs to prevent secondary reactions?**

   HFA was used to study kinetics of various SCIs in the past (e.g., Drozd et al., 2011; Drozd and Donahue, 2011). In these studies, HFA was implemented to directly probe SCI formation.

   We modify the following paragraph by specifying that HFA was used to prevent SCI secondary reactions (P4 L109):

   SCIs are known to be highly reactive towards ketones, especially electron poor ones such as HFA (Horie et al., 1999; ~~Drozd et al., 2011; Drozd and Donahue, 2011;~~ Taatjes et al., 2012). HFA has been previously used to effectively scavenge SCIs and prevent their secondary chemistry to directly probe SCI formation (Drozd et al., 2011; Drozd and Donahue, 2011).

2. **Page 6, Line 191-194 and Page 8, Line 249-251: Could the author give more detailed explanations or quantitative analysis for these four reasons?**

   We add the following details to our description (P6 L191):

   This discrepancy can be explained by a combination of the following factors~~(:)~~. First, a fraction of (CH₃)₂COO·HFA adducts might be irreversibly deposited on the surfaces inside the experimental setup and the PTR 8000 instrument (Pagonis et al., 2017). ~~wall losses of (CH₃)₂COO·HFA in the experimental setup and the PTR 8000 instrument; (2)~~ In addition, the sensitivity of observed SCI·HFA adducts depends on the reaction rate constant of the adduct with H₃O⁺ ion and the degree of fragmentation of protonated product ions SCI·HFA·H⁺ (Yuan et al., 2017). Since the reaction rate constant of SCI·HFA with H₃O⁺ ions is unknown, we assumed that all SCI·HFA adducts were

ionized via proton transfer from hydronium ions and therefore used the sensitivity we obtained from acetone calibration to quantify detected SCI·HFA species. In addition, we did not take into account possible fragmentation of SCI·HFA·H$^+$ ions which may impede their detection, although a first bond cleavage would likely only break the ozonide ring structure without loss of mass. ~~uncertainty in the sensitivity at which the SCI·HFA adducts were detected; (3) potential ion fragmentation of protonated SCI·HFA adducts; and (4)~~ *Finally, uncertainty of the kinetic model output is determined by the uncertainty in the SCI yield, and unimolecular and bimolecular reaction rate coefficients* ~~uncertainty in the SCI yield, and unimolecular and bimolecular reaction rate coefficients used in the kinetic model.~~

We add the following details to our description (P8 L248):

Similar to experiments described in Sect. 3.1, *several factors can contribute to this discrepancy: (1) gas-wall partitioning of RO$_2$ species and RO2·DMPO adducts in the* *experimental setup* ~~flow tube setup~~ *and inside the PTR3 instrument; (2) uncertainty in sensitivity at which RO$_2$·DMPO adducts were detected; (3) potential fragmentation of RO$_2$·DMPO·NH$_4^+$* *product ions*; *and (4) uncertainties in the reaction rate coefficient* k_{RO_2+DMPO}.

3. **Page 9, Line 277-278: Since there could be various RO$_2$ in ambient air, how does the author think about the feasibility of using the CID technique to measure ambient air?**

   The CID technique can be used to constrain the instrument sensitivity to compounds that cannot be calibrated directly, including dozens of oxygenated compounds that were produced during a photooxidation experiment in an environmental chamber (Zaytsev et al., 2019). While we plan to implement analytical techniques presented in this study for ambient measurements of atmospheric radicals in the future, we think that these experiments are out of the scope of the current work.

4. **Supplement page 8: In Figure S11, at the beginning of the period DMPO+O$_3$, why did the SCI adduct (m/z 315.228) get a little increasing?**

   There are two factors that could contribute to the increase of SCI·DMPO tracer (*m/z* 315.228) when DMPO and O$_3$ were present in the experimental setup:
   1. formation of an isomer with same molecular formula but potentially different structure
   2. change in humidity of sampled air which affects both primary ion signal and sensitivity to observed compounds. As one can notice, other tracers (e.g., $C_{16}H_{27}NO·NH_4^+$, *m/z* 154.160; $C_{16}H_{26}NO_5·NH_4^+$, *m/z* 330.216) also showed a little increase when ozone was introduced in the experimental setup.

5. **Page 8, Line 234 and Supplement page 2, Line7: The last two letters of the word "CH$_3$C(=O)CH$_2$OO" use two different fonts.**

   We thank the reviewer for spotting this typo and fix it in the revised manuscript.

References:

Pagonis, D., Krechmer, J. E., de Gouw, J., Jimenez, J. L., and Ziemann, P. J.: Effects of gas–wall partitioning in Teflon tubing and instrumentation on time-resolved measurements of gas-phase organic compounds, Atmos. Meas. Tech., 10, 4687–4696, DOI: 10.5194/amt-10-4687-2017, 2017.

Yuan, B., Koss, A.R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J.A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117, 13187–13229, DOI: 10.1021/acs.chemrev.7b00325, 2017.