

Interactive comment on “Measurements of the OH radical yield from the ozonolysis of biogenic alkenes: A potential interference with laser-induced fluorescence measurements of ambient OH” by Pamela Rickly and Philip S. Stevens

Anonymous Referee #2

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This manuscript describes tests performed on the LIF-FAGE instrument in use in the Indiana University to assess the presence of some interference species in the OH radical measurement. The tests performed within this study follow previous work from different LIF-FAGE groups and focus on the ozonolysis of different alkenes. The study shows that an interfering signal is observed during the ozonolysis of specific BVOC but extrapolating these results to ambient concentrations suggest that the interference coming from ozonolysis of unsaturated VOCs will have a negligible impact. I think the

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topic is of interest as it has been shown how different LIF-FAGE instruments (all with different instrumental parts, flows, etc) react differently to interfering species underlining the need of a characterization for each and every instrument. The manuscript is well written and structured though, in my opinion, it addresses the issue of the interference species insufficiently in-depth and it needs a more extensive characterization and analysis of the results.

A first general topic that needs to be address is a characterization of the titration unit used for the investigation of the interfering species. The literature cited when referring to the titration unit does not appear to give a full characterization of the device. As this paper focuses on the interference on the OH radical measurement and as the titration is currently in use in field campaigns, this would be the appropriate study to include the details about the titration unit such as losses on walls, plots with titration efficiency at ambient pressure and low pressure within the detection axis, dependency on the different parameters such as air flow, mixing volume, etc. This could be added in section 2.2.

The title of the manuscript is misleading. Neither in the abstract or in the conclusion OH radical yields from ozonolysis of selected alkenes are discussed as such. The study focuses mainly on the impact of the interference on the instrument rather than providing new insight in the OH yield. Therefore I feel there should be a more extensive analysis or discussion of possible interfering species. The interference from NO₃ as described by Fuchs et al. (2016) is mentioned but this would be the chance to actually perform tests in the laboratory to see how much this particular LIF-FAGE instrument is affected by it. The same is valid for other species as the study from Ren et al. (2004) applies to the LIF-FAGE instrument to which the tests were done. This is a good study to advance the knowledge on the interference species within the OH measurement of the LIF-FAGE by trying new/different possible trace gases.

Section 3.3 needs a lot more explanation and clarification: - It is not clear what the hypothesis of the authors is. The first paragraph of this section distinguishes between

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excited and stabilized Criegee intermediates mentioning that the first produce OH at short times (how short?) and the second at longer time (how long?). Are the authors arguing that the OH radicals they observed in the flow tube are only coming from the excited Criegee intermediates? If that is the case it should be stated explicitly. Though, it would be hard to explain how the OH would be formed within the instrument if the stabilized Criegee intermediates would not decompose within the flow tube. This assumption needs to be checked carefully as several studies conclude that the unimolecular decomposition rate of stabilized Criegee intermediates is rather fast (Smith et al., 2016; Chhantyal-Pun et al., 2016).

- The comparison of the signals as shown in Figure 7 is only valid if the OH formed within the flow tube originates from excited Criegee intermediates only. Formulas (for example, TOT signal = OHFlowTube (OHExcitedCriegee + OHStabilizedCriege + OHInterference) explaining clearly the expected component of every signal should be added to avoid confusion. If the OH observed in the flow tube also originates from stabilized Criegee intermediates it would not be possible to compare full red and full green symbols as the injection of acetic acid would remove a source, within the flow tube, for the OH observed.

- The comparison with the MCM 3.2 needs a lot more detail. The MCM mechanism as is does not include the chemistry needed to do a proper comparison, e.g. which unimolecular rate coefficient was used for the decomposition of the stabilized Criegee intermediate? On which assumptions/studies is the rate coefficient based? How do the authors deal with the fact that one of the two excited Criegee intermediates in the MCM does not decompose forming a stabilized Criegee intermediate (APINAOO)? How is the speciation of the 4 SCI formed from a-pinene treated (e.g. syn vs anti chemistry, relative yields, different unimolecular channels)? Are there additional losses included in the model for the SCI?

Figures need to be revised. In particular legends are not easy to understand rendering the message of the figure not very clear. I would recommend publication in AMT once

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these general points are addressed.

Specific comments:

Title: As suggested above, the title needs to be changed as the focus of the study is the study of the LIF-FAGE interference. The yield of OH radicals from the ozonolysis of BVOCs does not seem to be the main topic of the manuscript.

Page 2, Lines 9 to 16: The OP3 field campaign results (Whalley et al., 2011) needs to be added.

Page 2, Lines 21 to 27: Tests were done on a specific instrument, it needs mentioning.

Page 3, Line 20: The OH radical concentration measured with the LIF-FAGE agrees with the measurements performed with two CIMS instruments.

Page 3, Line 28 to 30: Here the text is misleading. Criegee intermediates decompose forming OH at low pressure and ambient pressure. Several experimental studies are now available proving the decomposition path and suggesting a rate (Smith et al., 2017; Kidwell et al., 2016; Fang et al., 2016) plus extensive theoretical material (see tables in Vereecken and Francisco (2012)).

Page 4, Line 21: Is this reaction time measured or calculated?

Page 4, Line 24: The majority of the tests described in this study include data points collected at 3 ozone values (I assume 1, 2 and 3 ppm). Was it not possible to explore a larger range of ozone values that would make the fit more robust? The accuracy of the ozone measurement needs to be added.

Page 4, Lines 26 on: Was any measurement done with, for example, a GC instrument to compare the calculated concentration of VOCs with the measured one? How were the losses on walls accounted for? What is the error on the estimated concentration? What are the concentrations for isoprene and MBO? A table summarizing the different experiments, at which conditions they were performed and the amount of interference

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observed would be helpful.

Page 5, Line 12 and 16: It is not clear which laser is the new one as both lasers have the same identification number.

Page 5, Line 20: Is there a particular reason to use a 12 m fiber in the laboratory? Do the authors expect a dependency of the interference on the length of the optical fiber?

Page 6, Line 1 to 2: How long does it take for the OH concentration to stabilize?

Page 6, Line 5: Why are the experiments performed in N2 and not synthetic air?

Page 6, Line 13: "the limit of detection was approximately between...". Summarizing the different sensitivity of the instrument for different parameters and inlet configuration in a table rather than a plot would be helpful and the error on the values should be stated.

Page 6, Section 2.2: As underlined above, a more in detailed characterization of the titration unit with figures of the scavenging experiments, wall losses values, dependency of the OH scavenging on the flow of air sampled, and on the mixing volume, etc., need to be added.

Page 7, Line 10: For which conditions was the steady state reached in 20 ms? The figures need to be self-explanatory. More text needs to be added in the figure caption together with a clearer legend.

Page 7, Line 16: For consistency: kO_3+VOC and $kOH+VOC$.

Page 7, Line 18: How much are k_{wall} and $kOH+O_3x[O_3]$ for the experiments performed in this study?

Page 7, Line 18: "measured as described in previous work by Handen et al., 2014..".

Page 7, Line 23: In figures 3 and 4, why are the data points with and without C3F6 added for a certain pressure in the cell at different ozone values? Those points are

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taken consequently or? Is the variation in the ozone due to instability of the ozone generator? Is one data point in the plot the average of a single experiment or the average of the repetition of different experiments performed at the same conditions? What kind of fit is applied? Is it weighted on the errors? Does it account for errors on both x and y axis?

Page 8, Line 9: The fit showed in the central and bottom panel of figure S3 hardly represents the data. Was here used a different fit? Is there an explanation for the extremely higher values for the interference for the long inlet with the 1 mm pinhole (bottom panel figure S3) compared to the values observed for the same inlet with the 0.6 mm pinhole (bottom panel figure 3)? The values for the other two inlet lengths did not show a drastic variation between the 2 different pinholes. Could this be related to a smaller drop in sensitivity observed between medium and long inlets with the 1 m pinhole compared to the 0.6 mm one?

Page 8, Line 14: "The different pressures in these experiments..."

Page 8, Line 15: Remove likely

Page 8, Lines 18 to 20: The longer inlet will also increase the OH losses so it is still not clear why with the longer inlet there is an increase of interference when increasing the pressure.

Page 8, Lines 20 to 21: A legend should be added to figure 4 together with the errors on the concentrations of the BVOC.

Page 8, Lines 27 to 28: By looking at figure 4 central panel it is possible to observe a trend with higher concentration of interference for higher concentration of β -pinene.

Page 8, Line 30: Which Ocimene isomer was used during the experiments?

Page 9, Line 9: Remove likely.

Page 9, Line 14: Was the expected steady state concentration of OH radicals for the

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condition of the experiments calculated? Rate coefficient of Isoprene with O₃ is less than a factor of 2 slower than the one with β -pinene and the tabulated OH yields are similar for both (~ 0.25) so it is not clear why there would not be any detectable OH signal especially at the highest ozone concentration.

Page 10, Line 10: To which experiments does "These experiments" refer to?

Page 10, Line 15: Use molecules cm⁻³ for the x axis as in the previous plots. Here it would be interesting to also have in a figure the amount of interference from β -pinene and ocimene.

Page 10, Line 18: Ocimene and β -pinene should be added to Figure 6 to see if they lie on the same line as it is shown in Fuchs et al. (2016). The possible explanation about the large scatter observed in the data should also be given. How does the plot look like for longer inlets?

Page 10, Line 24 on: Here a table including also β -pinene (or is there a reason not to list it?) could substitute the plots.

Page 11, Line 3 on: The last paragraph is difficult to understand. I see what point the authors want to make (although I am not sure this is the appropriate place in the manuscript to make this point) but the text could benefit from rephrasing.

Page 11, Lines 11 to 15. Criegee intermediates can also be formed directly in a stabilized form from non-endocyclic double bonds. It would also be helpful at this stage to give an estimate of the time scale where these CI give OH, i.e. stabilized CI of the order of milliseconds, collisional stabilisation is of the order of 10⁸ s⁻¹, prompt decomposition is thus at even faster rates, also implying a very low steady state concentration of excited CI. The OH concentrations are not in steady state because the excited CI are in steady state: these two species have different formation and destruction timescales, where excited CI will reach steady state concentration orders of magnitude faster than OH. It also needs to be specified that the steady state is reached only within the flow

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tube and not inside the instrument. In the conclusions the authors also suggest that SCI decomposition may not be constant throughout the detection cell, e.g. more SCI migrating to the walls and only then undergoing decomposition. Such effects should also be discussed in more detail at the start so a complete kinetic model is available prior to interpreting the results.

Page 12, Line 5: Was it not possible to try different SCI scavengers like water and/or SO₂?

Page 12, line 24 to 26. The modeling of the concentration of excited CI should go to the section at the end of page 11 to further strengthen the assertion that excited CI cannot be the source of the interference. This should also be stated explicitly.

Page 12, Lines 28 "Criegee..".

Page 13, Lines 2 to 3: Chao et. al 2015 measured a fast rate coefficient for CH₂OO with water dimers but it is not a good idea to generalize this rate for all the Criegee intermediates as several studies (see Vereecken et al. (2015) and citations therein) have shown that the rate with water and water dimers will strongly depend on the structure of the Criegee intermediates.

Page 13, Line 6: The authors discuss the potential impact of using alkene ozonolysis on FAGE calibration. It could be beneficial to separate that out in a separate paragraph or even a separate section.

Page 14, Line 14: The Isoprene concentration is mentioned as indicative on the likelihood of interferences in this specific LIF-FAGE instrument but as no interference was observed for concentrations way larger than what observed in the field it does not seem to be the appropriate parameter.

Page 14, Line 23: What was the percentage of the interference compared to the "real" atmospheric OH? How much was the known ozone interference?

Page 14, Lines 29 to 31: Any hypothesis on what could be the cause for the interfer-

ence?

Page 15, Lines 8 to 10: This sentence is correct if contemporary to the addition of Acetic acid also C3F6 was injected and no OH signal was observed. Was this the case?

Page 15, Lines 18 to 20: Trying to minimize any interference is important, but isn't this specific interference actually, probably, not so relevant in field campaigns? Is there going to be a gain in modifying the instrument for a negligible interference risking losing in sensitivity or encountering different problems? Are there tests showing that the modification improve the quality of the OH measurement?

References:

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- Fang, Y., Liu, F., Klippenstein, S. J., and Lester, M. I.: Direct observation of unimolecular decay of CH₃CH₂CHO_O Criegee intermediates to OH radical products, *The Journal of Chemical Physics*, 145, 044312, doi:<http://dx.doi.org/10.1063/1.4958992>, 2016.
- Fuchs, H., Tan, Z., Hofzumahaus, A., Broch, S., Dorn, H. P., Holland, F., Künstler, C., Gomm, S., Rohrer, F., Schrade, S., Tillmann, R., and Wahner, A.: Investigation of potential interferences in the detection of atmospheric ROx radicals by laser-induced fluorescence under dark conditions, *Atmos. Meas. Tech.*, 9, 1431-1447, 10.5194/amt-9-1431-2016, 2016.
- Kidwell, N. M., Li, H., Wang, X., Bowman, J. M., and Lester, M. I.: Unimolecular dissociation dynamics of vibrationally activated CH₃CHO_O Criegee intermediates to OH radical products, *Nat Chem*, advance online publication, 10.1038/nchem.2488

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