Response to Anonymous Referee #1

We would like to thank the reviewers for their efforts in reviewing this manuscript, and we feel that the manuscript is much stronger with the suggested changes. Below are detailed responses to their comments, which are highlighted in italics.

I was very interested to review this manuscript which falls well within the scope of AMT and reports on the extremely important subject of potential OH artefacts in LIF instruments used for ambient OH measurements. Although other LIF groups have reported their findings from their own LIF instruments (Mao et al, Novelli et al and Fuchs et al), it is very important for the experiments presented in this manuscript to be conducted and published by every LIF group involved in ambient OH detection. In this manuscript there are a few key experimental details missing in places, particularly the Inlet Pre Injector parameters, which need to be included in the revised manuscript (discussed below). I also have some concerns over the experimental approach (which will likely be resolved once further experimental detail is provided) and the presentation of the results could be improved upon. Notwithstanding, once these changes are made I fully recommend publication in AMT.

Specific comments

Abstract: In general there needs to be further specific details on the key findings included in the abstract.

Line 16: 'several BVOCs..' these should be named in here

We have added the names of each of the BVOCs measured to the abstract as suggested.

Line 18: 'an interference under high ozone and BVOC concentrations was observed..' It is important to state the level of the interference in the abstract. I understand that this level varied with [O3] and [BVOC] and BVOC type, but I suggest reporting the maximum interference observed and giving the concentration of the pre-cursors for a particular experiment. It is also important to state here the anticipated interference under ambient conditions somewhere in the abstract.

As suggested, we have added the average level of the interference observed and the range of precursor concentrations to the abstract. We have also added a statement concerning the anticipated interference under ambient conditions.

Pg 2, lines 28-30: Mention specific chemical condition under which the measurements were made.

We have added that the measurements were made under varying concentrations of of H_2O, O_3, CO, HCHO, NO, and NO_2 as described in Schlosser et al., 2007.

Pg 4, lines 10-11: What is the motivation for choosing these specific BVOCs? Has ocimene been observed at appreciable levels in forested environments?

The BVOCs chosen represent major monoterpene emissions (α- and β-pinene) as well as a frequent emission (cis-ocimene) (Guenther et al., Atmos. Environ., 28, 1197-1210, 1994), in addition to isoprene and MBO. This has been clarified.

Pg 5, line 2: Although no OH or artefact signal was observed during experiments conducted with isoprene and MBO, the experimental conditions, i.e. the concentration of isoprene and MBO (and ozone concentration if different from the other ozonolysis experiments) should be added to the experimental section.

We have added the approximate concentrations of both isoprene and MBO used in these experiments to the experimental section as suggested.

Section 2.1: It is unclear which laser was used for the experiments detailed in this manuscript.

This has been clarified in the revised manuscript.

How do the pressures tested in these experiments compare to those typically employed during ambient measurements?

We have clarified the normal operating pressures and inlet lengths typically used during previous ambient measurements as suggested.

Section 2.2: The authors need to provide additional details on their chemical titration scheme. Specifically, what is the total flow rate through the chemical titration section of the instrument? What is the concentration of C3F6 added (in molecule cm-3)? What is the residence time of gas in the chemical titration section? These parameters are important as I worry that if only 90% of a point OH source (from the calibration wand) is removed by the scavenger, then even less OH generated via a steady state source (O3+BVOC) will be removed and this could lead to a bigger percentage of the OH signal observed being assigned as an interference than is necessarily the case. Other experimental results presented, such as the agreement of the OH yield with literature values, and the variation in the magnitude of the interference with inlet length do suggest that the amount of scavenger injected is sufficient to remove a steady state source of OH, but it is important to demonstrate this absolutely. The authors could consider presenting results from a simple kinetic model which includes the main OH source (O3+alkene) and sink reactions (OH+alkene, OH+C3F6 reaction), run over the residence time in the chemical titration section, to demonstrate this?

We have expanded the description of the chemical titration scheme in this section, including a schematic diagram of the injector ring in Figure 2. We have also included estimates of the concentration of C_3F_6 added and the residence time in the titration region as suggested. We have also provided results of a simple kinetic model, which shows that the amount of C_3F_6 added and the residence time in the titration region, is enough to reduce the steady-state concentration of OH from the ozonolysis reactions to below the detection limit of the instrument for the majority of the experiments described here. However, it is possible that for some of the high concentration experiments, the amount of C_3F_6 added may not have been sufficient to reduce the steady-state concentration of OH to below the detection limit, especially for the ocimene experiments due to the high reactivity of ocimene with ozone. However, the model simulations suggest that even for these high concentration experiments the remaining steady-state OH concentrations represented less than 10% of the observed interference. This has been clarified in the revised manuscript.

Pg 8, lines 27, 28: There does seem to be some trend with beta-pinene concentration?

We have added a statement indicating that there appears to be a trend in the measured OH yield with increasing β-pinene concentration.

Pg 9, line 15: As well as reflecting the 'higher reactivity' of the mono-terpenes with ozone compared to isoprene and MBO, important also (to the real OH signal) is relative reactivity of BVOC+O3 vs BVOC+OH (and the OH yield from ozonolysis). All should be mentioned as possible reasons for the lack of real OH signal observed. I am a little surprised that no OH signal was observed during these experiments even with the shortest inlet given the limit of detection stated in section 2.1.

We have clarified that the lower expected steady-state OH concentration in the ozonolysis of isoprene and MBO are lower due to the relative reactivity with ozone and OH as well as the overall OH yield as suggested. We have also performed simulations that show that the expected OH concentration in the isoprene experiments were approximately 50 times lower than that for the α-pinene experiments, consistent with a lower steady-state OH concentration estimated using Equation 1, and near or below the detection limit of the instrument.

Is the concentration of SCI in the isoprene+O3 and MBO+O3 experiments estimated to be lower than during the monoterpene+O3 experiments? The rate coefficients, kisop+o3 and kbetapinene+o3 are similar.

As pointed out by the reviewer, simulations using the Master Chemical Mechanism suggest that the concentration of SCIs in the isoprene + O_3 experiments is similar to that in the α-pinene + O3 experiments. This may suggest that a similar interference should have been observed during the isoprene experiments as was observed during the α-pinene experiments. Given that OH yield from the decomposition of excited CIs in the isoprene mechanism is lower than that for the α-pinene mechanism, the absence of a detectable interference in the isoprene experiments described here may suggest that the decomposition of these intermediates inside the FAGE detection cell may also be slower. As a result, the observed interference for each alkene is likely proportional to the OH yield from the ozonolysis mechanism. This is consistent with the observation that the observed interference appears to be a constant fraction of the total OH yield in these experiments independent of the ozone concentration and the turnover rate (Figs. S5 and S6). This has been clarified in Section 3.3 of the revised manuscript.

Pg 10, lines 27- 30: It is interesting/perplexing that the artefact signal is actually lower when the medium inlet is used than when the shorter inlet is used. In light of previous results (Fuchs et al. 2016) which demonstrated a dependence of the magnitude of the artefact signal on cell residence time a comment on the lack of trend in level of interference and inlet length is needed here.

As pointed out by the reviewer, the level of the observed interference is similar for the short and medium length inlet, but increases with the longest inlet. This suggests that the level of interference is not directly related to the residence time inside the FAGE detection cell, but may be the result of increased collisions with the interior surfaces of the detection cell that occurs when using the longest inlet. We have clarified this here, as well as in the previous discussion in Section 3.1.

Section 3.3: The working hypothesis on the identity of the observed OH interference is that it derives from the decomposition of a SCI. Were any experiments conducted with alkene concentration in excess? Under these conditions the concentration of the SCI would be maximised, whilst the concentration of externally generated OH from ozonolysis would be small, meaning that the artefact signal should be readily distinguishable from a real OH signal?

Unfortunately, due to the low vapor pressures of these compounds we were unable to generate high enough concentrations of the alkenes to conduct experiments with them in excess.

Pg 12, lines 1 – 17: What was the concentration of acetic acid added to the flow-tube? Would any loss of OHss by reaction with acetic acid be expected given the residence time?

For these experiments, approximately 9×10^{12} molecules cm^3 of acetic acid was introduced into the flow tube and allowed to react for approximately 200 ms. At this concentration, the reaction with acetic acid was modeled to have a minimal impact on the steady-state concentration of OH, as the rate constant for the OH reaction is approximately 7×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. This has been clarified in the revised manuscript.

Pg 12, lines 22 – 24: 'Based on these results, the observed OH interference in these experiments could be explained if approximately 5% of these intermediates dissociated..'Does this then effectively disprove the hypothesis that the transmission efficiency of SCI vs OH through the pinhole is substantially different? A comment on transmission efficiency assumed for these lab results vs transmission efficiency estimated from field results (and the implications of these differences) would be welcomed in the revised manuscript.

It's not clear whether the results of these experiments and modeling disproves the hypothesis that the transmission efficiency of SCIs are substantially different than that for OH, as it is possible that the transmission efficiency of SCIs through the inlet is high, but only 5% of those entering the detection cell actually dissociate into OH.

In these experiments, as well as in field studies, we are assuming that the transmission efficiency of SCIs is essentially 100% and similar to the transmission efficiency of OH. This is based on previous measurements of the loss of OH on different inlet designs and coatings on a similar LIF instrument inlet, as well as measurements of the calibration factor with and without the inlet, suggest that heterogeneous loss of OH on the inlet is minimal (Stevens et al., 1994). This has been clarified in Section 3.3 of the revised manuscript.

Technical corrections

Pg 2, line 26: 'their' to 'Penn State'

Added as suggested

Pg 4, line 15: add ' with sliding injector' after 'flow tube' so the later discussion on the injector is easier to follow.

Added as suggested.

Pg 4, line 17: Define 'IU-FAGE'

Defined as suggested.

Pg 6, line 20: add ' compared to chemical modulation' after 'spectral modulation'?

Added as suggested

Pg 6, line 21: change 'reflect' to 'can reveal'?

Changed as suggested.

Pg 6, line 25: is this 3 – 5 sccm of 1% C3F6 in N2 or 3 – 5 sccm pure C3F6?

This has been clarified as 3-5 sccm of 99.5% C_3F_6.

Pg 9, line 7: ±0.9 is a very large error. Is this correct?

The actual error is ±0.09 and has been corrected.

Pg 10, line 19: Define 'turnover time'

We have defined the turnover time as the steady-state rate of OH radical propagation, expressed as the alkene ozonolysis rate.

Figures: Stick to [O3] in molecule cm-3 or ppm.

We have converted all graphs to concentration units, as suggested.

Figure 3 – 7: Axes should be rescaled and legends should be made more selfexplanatory. It took me a while to understand what 'Pcell 4' actually represented.

We have rescaled the graphs and have clarified the legends to make them more self-explanatory, as suggested.

Figure 3 & 4: It isn't clear to me why the OH yield from the ozonolysis reactions and the OH signal without scavenger are on the same graph? They are two distinct results that just happened to have been determined in the same experiment. I am struggling to suggest a better way to present the results, but maybe the authors could critically review these figures before final publication?

We included the OH yield from the ozonolysis reactions with the measured OH signal without the C_3F_6 scavenger to illustrate the magnitude of the measured interference. We have clarified this reasoning in section 3.1 of the revised manuscript.

Figure 4: Include a legend on this figure that clearly states the VOC concentration for the different experiments, e.g. green = x cm-3

We have modified the legend to include the VOC concentrations for each experiment as suggested.

Figure 5: it is not obvious to me why these three panels are grouped together? The recommendations for improving the figures above should be considered for the figures included in SI also.

We have grouped the panels in Figure 5 together for simplicity, similar to Figure 6 in Fuchs et al., 2016. We have also changed the figures in the Supporting Information, as suggested.

Response to Anonymous Referee #2

We would like to thank the reviewers for their efforts in reviewing this manuscript, and we feel that the manuscript is much stronger with the suggested changes. Below are detailed responses to their comments, which are highlighted in italics.

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 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.

We have expanded the description of the chemical titration scheme in this section, including a schematic diagram of the injector ring in Figure 2 as suggested. We have also included a discussion of potential wall losses and the impact of the titration efficiency on the airflow from different inlets.

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.

We have changed the title of the manuscript as suggested to "Measurements of a potential interference with laser-induced fluorescence measurements of ambient OH from the ozonolysis of biogenic alkenes" as suggested. We hope that this new title will more clearly reflect the overall topic of the paper. Although we agree that additional measurements of potential interferences from other species is needed, we feel that these measurements are beyond the scope of the present paper, which is focused on an interference that may be common to ambient measurements of OH by LIF-FAGE instruments in environments

impacted by biogenic emissions as observed by several groups (Mao et al., 2012; Novelli et al., 2014). Future experiments will involve measurements of potential interference from other species, including NO_3 radicals.

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 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 check 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).

We have attempted to clarify the two hypotheses for the source of the interference by separating section 3.3 into two subsections in the revised manuscript. The first subsection (3.3.1 Decomposition of Criegee intermediates produced inside the FAGE detection cell as a source of the interference) attempts to determine whether the source of the interference is due to the production of Criegee intermediates from ozonolysis inside the FAGE detection cell. We have clarified the approximate reaction times associated with OH production from excited Criegee intermediates and stabilized Criegee intermediates as suggested based on the measurements by Kroll et al. (2001), which could explain the observed dependence of the interference on the inlet length and reaction time in the detection cell. However, as discussed in the manuscript, it is unlikely that the interference is due to internal production of Criegee intermediates due to the short reaction time and reduced concentrations of ozone and the alkene.

The second subsection (3.3.2 Decomposition of Criegee intermediates produced outside of the FAGE detection cell as a source of the interference) discusses the possibility that the interference is due to stabilized Criegee intermediates produced from ozonolysis in the flow tube that enter the low pressure FAGE detection cell and decompose into OH radicals. As mentioned in the manuscript, previous measurements have demonstrated that stabilized Criegee intermediates can decompose inside the low pressure region of the FAGE detection cell leading to the formation of OH radicals (Novelli et al., 2014). The experiments involving the addition of acetic acid to the flow tube suggest that the interference is due to stabilized Criegee intermediates produced external to the FAGE detection axis.

As pointed out by the reviewer, the results of these experiments suggest that the majority of the OH radical concentrations observed in the flow tube experiments is due to the rapid decomposition of excited Criegee intermediates, and this has been clarified in the revised manuscript. If all of the OH produced from the flow tube came from the decomposition of stabilized Criegee intermediates, then the OH signal measured in the presence of acetic acid would be less than the measured OH after the interference was subtracted. However, these results do not exclude the possibility that SCIs are also thermally decomposing and contributing to OH production in the flow tube. As pointed out by the reviewer, a decomposition rate of SCIs that is similar to that measured by Smith et al. (2016) and Chhantyal-Pun et al. (2017) could also compete with reaction of this intermediate with acetic acid. Additional experiments beyond the scope of this paper are needed to determine whether stabilized Criegee intermediates contribute to OH radical production in the ozonolysis mechanisms of these biogenic compounds. This has been clarified in the revised manuscript. However, the absence of OH production from stabilized Criegee intermediates in the atmospheric pressure flow tube does not preclude OH production from these intermediates inside the low pressure FAGE detection cell. The increased collisions with the walls of the

cell as well as the supersonic shock that occurs as the air stream expands into the low pressure region may provide the conditions necessary for dissociation of these intermediates into OH radicals.

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.

We agree that the results of the experiments suggest that the majority of the OH formed within the flow tube originates from excited Criegee intermediates, and as discussed above this has been clarified in the revised manuscript. Because these experiments cannot distinguish between OH produced in the flow tube from excited or stabilized Criegee intermediates, we have chosen not to separate these components in a formula for simplicity.

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 intermediates (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?

We have added additional details describing the α-pinene ozonolysis mechanism in the MCM as suggested. This version of the MCM does not include a mechanism for the formation of OH from the stabilized Criegee intermediate, nor does it distinguish between the syn and anti isomers of the Criegee intermediates. No additional reactions were added to the model. Despite its shortcomings, the MCM was used to provide a rough estimate of the concentration of Criegee intermediates to compare with the experimental measurements for simplicity.

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 these general points are addressed.

We have revised the figures both in the main manuscript as well as in the supplementary information as suggested. In particular, we have clarified the legends so that they are easier to understand.

Specific comments:

Title: As suggested above, the title needs to be change 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.

As mentioned above, we have changed the title to more clearly reflect the overall topic of the paper.

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

We have included the results from the OP3 campaign in the introduction as suggested.

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

We have clarified that these tests were done on the Penn State instrument.

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

We have clarified this as suggested.

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)).

We clarified in this discussion that Criegee intermediates can decompose at ambient pressure, and have included the references as suggested.

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

The reaction time was calculated based on measurements of the flow velocity. This has been clarified.

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.

Unfortunately, the ozone generator used in these experiments provided the highest stability at these concentrations and this is why most of the experiments were done at these three concentrations. We have clarified this in the revised manuscript and have included an estimated uncertainty associated with the ozone measurements.

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?

Unfortunately, no direct method for measuring the concentration of these BVOCs was available, and as a result the absolute concentration of BVOCs in the flow tube is highly uncertain due to potential wall losses prior to entering the flow tube. This has been clarified in the revised manuscript.

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 observed would be helpful.

We have included the estimated concentrations for isoprene and MBO in the revised manuscript, and have included a table summarizing the conditions of the different experiments in the Supplementary Information.

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

We clarified which of the two laser systems was used in these experiments.

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?

We use a 12 m fiber for these experiments as that is the fiber length used in most field measurements by our instrument. Different fiber lengths result in different reflections from the ends of the fiber, which impacts the background signal. We do not expect that the interference would depend on the length of the fiber.

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

We have clarified that it took several minutes for the OH concentration to stabilize, primarily due to stabilization of the generated ozone concentration.

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

Nitrogen from liquid boil-off was used instead of air to reduce the concentration of reactive impurities in the system. This has been clarified in the revised manuscript.

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.

We have included a table in the Supplementary Material summarizing the sensitivity and limits of detection for the different experimental parameters, as suggested. We have also included a statement in the revised manuscript on the estimated uncertainty associated with the UV-water photolysis calibration method (± 36%, 2σ).

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.

As discussed above, we have expanded the description of the chemical titration scheme, including a schematic diagram of the injector ring in Figure 2 as suggested. We have also included a discussion of potential wall losses and the impact of the titration efficiency on the airflow from different inlets. Experiments conducted under different lengths of the injector above the inlet did not reveal any loss of ambient OH or improvement in the scavenging efficiency, nor was any change in the scavenging efficiency observed on the flow of air sampled for the two inlet diameters. This has also been clarified in the revised manuscript.

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.

Computer simulations indicated that under the BVOC and ozone concentrations used in these experiments, the OH concentrations reached steady state in less than 20 ms. This has been clarified in the revised manuscript.

Page 7, Line 16: For consistency: kO3+VOC and kOH+VOC.

This has been changed as suggested.

Page 7, Line 18: How much are kwall and kOH+O3x[O3] for the experiments performed in this study?

We have added the loss rates due to reaction with the wall and with ozone to the revised manuscript as suggested.

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

This has been changed as suggested.

Page7, Line 23: In figures 3 and 4, why are the data point with and without C3F6 added for a certain pressure in the cell at different ozone values? Those points are 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?

As pointed out by the reviewer, the points with and without C_3F_6 addition in these plots appear at different ozone values due to the instability of the ozone generator. Each measurement was repeated several times and the points represent averages of the measurements. During the measurements, variations in the ozone concentration produced by the generator led to the variations in the measured ozone concentration. This has been clarified in the revised manuscript.

The measured OH yields were determined from a weighted fit of the slope of the plot of the OH concentration versus ozone concentration. The weights are determined from the precision of the measurements of both OH and ozone. This has also been clarified in the revised manuscript.

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 length 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?

The lines in the plots do not represent the weighted fits of the data, but represent the expected OH concentrations as a function of ozone concentration based on recommended yields for each reaction. This has been clarified in the revised manuscript.

The larger interference observed with the larger 1mm nozzle diameter and the long inlet length is likely due to the longer reaction time inside the detection cell, resulting in greater collisions with the wall of the longer inlet. This has been clarified in the revised manuscript.

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

This has been changed as suggested.

Page 8, Line 15: Remove likely

This has been removed as suggested.

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.

As pointed out by the reviewer, the longer inlet also increases the wall loss of OH radicals in the detection cell. Losses of OH produced outside of the detection cell are accounted for during the calibration of the instrument, but losses of OH produced inside the detection cell are not. As a result, the observed interference likely represents a lower limit to the actual interference produced in the detection cell. One possible explanation of the observation of an increased interference with the longer inlet is that the loss of

OH is less than rate of production of the interference under these conditions. This has been clarified in the revised manuscript.

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

We have added a legend listing the estimated BVOC concentrations. As discussed above, these estimated concentrations are highly uncertain given potential losses prior to entering the flow tube. This has been clarified in the revised manuscript.

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.

We have added a statement indicating that there appears to be a trend in the measured OH yield with increasing β-pinene concentration.

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

The ocimene used in these experiments contained a mixture of isomers. This has been clarified.

Page 9, Line 9: Remove likely.

This has been removed as suggested.

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

We have clarified that the lower expected steady-state OH concentration in the ozonolysis of isoprene and MBO are lower due to the relative reactivity with ozone and OH as well as the overall OH yield. We have also performed simulations that show that the expected OH concentration in the isoprene experiments were approximately 50 times lower than that for the α-pinene experiments, consistent with a lower steady-state OH concentration estimated using Equation 1, and near or below the detection limit of the instrument. This has also been clarified in the revised manuscript.

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

This has been clarified.

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.

We have changed the units in this figure as suggested, and have added the results from the ocimene experiments to this plot.

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?

We have added the results for ocimene and β-pinene to Figure 6 as suggested. The large scatter observed in the data are likely due to the large uncertainty associated with estimates of the BVOC concentrations in these experiments. However, the level of the observed interference is greater than that illustrated in Fig. 6

for the measurements using the long inlet, suggesting the similarity with the results of Fuchs et al. (2016) may be fortuitous, as differences in the design of the instrument impacts the level of the interference. In contrast to the results of Fuchs et al., the level of interference as a function of the turnover rate is not similar for all of the BVOCs tested. While the observed interference as a function of turnover rate appears to be similar for the ozonolysis of α-pinene and ocimene, the observed interference for the ozonolysis of β-pinene is significantly less. This may also be related to uncertainties associated with estimates of the concentration of β-pinene in the flow tube, but may also suggest differences in the mechanism for the production of the interference for some BVOCs. Additional measurements of the interference for other BVOCs are needed to resolve this discrepancy. These issues have been clarified in the revised manuscript.

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.

We have included a table summarizing the measurements in Figure S5 in the Supplementary Material as suggested.

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.

We have rephrased this paragraph as suggested.

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 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.

We have added information regarding the estimated rates of decomposition of both excited Criegee intermediates and stabilized Criegee intermediates to this section as suggested, and have specified that the OH radical reaches steady-state in the flow tube rather than inside the detection cell in the following paragraph, as suggested. We have also included a statement clarifying that the lifetime of SCIs inside the low pressure detection cell may be long enough for wall collisions, as suggested.

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

Acetic acid was chosen over SO_2 as an SCI scavenger as SO_2 fluorescence at 308 nm can interfere with OH measurements (Fuchs et al., 2016). Addition of water in the presence of the high concentrations of ozone in these experiments would have led to significant laser-generated OH from the photolysis of ozone followed by reaction of the $O(^1D)$ product with water vapor. This has been clarified in the revised manuscript.

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.

The modeled concentration of the excited CI in this section refers to the steady-state concentration achieved under the concentrations of ozone and the alkene in the flow tube, which are much greater than the concentration inside the detection axis. Because the discussion at the end of page 11 in the original manuscript addresses the production of excited CI inside the detection axis, we have not moved this discussion. We have stated explicitly in both sections that excited CI cannot be the source of the interference as suggested.

Page 12, Lines 28 "Criegee..".

This typo has been corrected.

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.

We have clarified this in the revised manuscript, as suggested.

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.

As suggested, we have created a separate section in the revised manuscript discussing the potential impact of interferences associated with using the alkene ozonolysis technique to calibrate LIF-FAGE instruments.

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.

We have clarified this discussion to focus on how the difference in temperature between the different field campaigns likely led to different BVOC concentrations, using isoprene as an indicator of this difference.

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

During this campaign, all interferences accounted for approximately 60% of the total measured OH signal on average. The known interference from laser-generated OH varied with laser power, ambient ozone and water concentrations, but was approximately half of the total measured interference on some days, while on other days accounted for all of the measured interference. These results will be summarized in a future publication, but we have added this information to the revised manuscript as suggested.

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

Similar to that discussed in Novelli et al. (2016), the results of these measurements does not allow for an unequivocal identification of the source of the interference, although it may be possible that the interference observed during ambient measurements may be due to the ozonolysis products of BVOCs not

tested in the experiments reported here. This hypothesis has been added to the revised manuscript as suggested.

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?

Unfortunately we did not conduct tests where both acetic acid and C_3F_6 were added simultaneously. However, the observation that the measured OH concentrations after addition of acetic acid were similar to measurements when the interference was subtracted and suggests that the interference in these experiments is due to stabilized Criegee intermediates. This sentence has been revised to clarify this point.

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?

Based on estimates of stabilized Criegee concentrations in the ambient atmosphere, it appears that the interference characterized in these experiments may not be relevant in field campaigns. However, it is possible that other unknown interferences may have a similar dependence on instrument parameters. We have revised this statement to reflect that tests will be done to minimize the observed ambient interference though changes in both reaction time and potential surface collisions, while also maintaining the quality of the ambient OH measurement.

Measurements of a potential interference with laser-induced fluorescence measurements of ambient OH from the ozonolysis of biogenic alkenes

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Abstract. Reactions of the hydroxyl radical (OH) play a central role in the chemistry of the atmosphere, and measurements of its concentration can provide a rigorous test of our understanding of atmospheric oxidation. Several recent studies have shown large discrepancies between measured and modeled OH concentrations in forested areas impacted by emissions of biogenic volatile organic compounds (BVOCs), where modeled concentrations were significantly lower than measurements. A potential reason for some of these discrepancies involves interferences associated with the measurement of OH using the Laser-Induced Fluorescence - Fluorescence Assay with Gas Expansion (LIF-FAGE) technique in these environments. In this study, a turbulent flow reactor operating at atmospheric pressure was coupled to a LIF-FAGE cell and the OH signal produced from the ozonolysis of α-pinene, β-pinene, ocimene, isoprene, and 2-methyl-3-buten-2-ol (MBO) was measured. To distinguish between OH produced from the ozonolysis reactions and any OH artefact produced inside the LIF-FAGE cell, an external chemical scrubbing technique was used, allowing for the direct measurement of any interference. An interference under high ozone (between 2-10 × 10^{13} cm^{-3}) and BVOC concentrations (between approximately 0.1 – 40 × 10^{12} cm^{-3}) was observed that was not laser generated and was independent of the ozonolysis reaction time. For the ozonolysis of α- and β-pinene, the observed interference accounted for approximately 40% of the total OH signal, while for the ozonolysis of ocimene the observed interference accounted for approximately 70% of the total OH signal. Addition of acetic acid to the reactor eliminated the interference, suggesting that the source of the interference in these experiments involved the decomposition of stabilized Criegee intermediates inside the FAGE detection cell. Extrapolation of these measurements to ambient concentrations suggests that these interferences should be below the detection limit of the instrument.

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1. Introduction

The hydroxyl radical (OH) plays an important role in the chemistry of the atmosphere. OH initiates the oxidation of volatile organic compounds (VOCs) which in the presence of nitrogen oxides (NO_x) can lead to the production of ozone and secondary organic aerosols, the primary components of photochemical smog. Because of its high reactivity, measurements of OH can provide a rigorous test of our understanding of the fast radical chemistry in the atmosphere. However, several field campaigns have identified significant discrepancies between measured and modeled OH concentrations, especially in low NO_x forested environments (Rohrer et al., 2014). For example, Ren et al. (2008) found that OH concentrations were well predicted by models to within their combined estimated uncertainty when mixing ratios of isoprene were less than approximately 500 pptv, but measurements acquired in areas with higher mixing ratios of isoprene showed observed OH concentrations that were 3-5 times larger than model predictions. Similarly, measurements in a northern Michigan forest found daytime OH concentrations approximately three times larger and nighttime concentrations 3-10 times larger than model predictions (Tan et al., 2001; Faloona et al., 2001). Aircraft measurements over the Amazon rainforest found OH concentrations to be 40-80% larger than model predictions (Lelieveld et al., 2008), while measurements of OH in the Borneo rainforest were 5-10 times greater than model predictions (Whalley et al., 2011). Similarly, measurements of OH concentrations under high mixing ratios of isoprene in the Pearl River Delta, China were 3-5 times larger than model predictions (Hofzumahaus et al., 2009).

Most of these measurements were done using the Laser-Induced Fluorescence – Fluorescence Assay by Gas Expansion (LIF-FAGE) technique. In this technique, ambient air is sampled through an inlet at low pressure, enhancing the OH fluorescence lifetime and allowing temporal filtering of the OH fluorescence from laser scatter (Heard and Pilling, 2003). Fluorescence from OH radicals is distinguished from background scatter and broadband fluorescence through spectral modulation of the laser wavelength. Previous laboratory tests using the Penn State instrument demonstrated that the technique was free from interferences from several species, including spectral interferences from naphthalene, sulfur dioxide, and formaldehyde as well as chemical interferences from high concentrations of H_2O_2, HONO, SO_2, HNO_3, several alcohols and alkanes, propene, and isoprene (Ren et al., 2004). Mixtures of ozone with ethene, propylene and isoprene did not result in any significant signal, suggesting that the ozonolysis of these compounds did not produce an interference in the Penn State instrument, although small interferences were observed with addition of high amounts of ozone and acetone that would be insignificant under ambient conditions (Ren et al., 2004). Measurements of OH in the SAPHIR chamber at atmospheric pressure and under varying concentrations of H_2O, O_3, CO, HCHO, NO, and NO_2 by both an LIF-FAGE instrument and a differential optical absorption spectroscopy (DOAS) instrument were in excellent agreement,

suggesting that measurements of OH using the LIF-FAGE instrument were free from artifacts under these conditions (Schlossler et al., 2007). A subsequent intercomparison inside the SAPHIR chamber found that measurements from several different LIF-FAGE instruments under a variety of conditions agreed with each other to within the calibration accuracies of the instruments (Schlosser et al., 2009). No interferences were detected under varying concentrations of O_3, H_2O, NO_x and peroxy radicals, and measurements of OH during the ozonolysis of various mixing ratios of pent-1-ene (6-25 ppb) and trans-2-butene (200 ppb) in approximately 100 ppb of ozone also did not reveal a significant interference (Schlosser et al., 2009). In contrast, Hard et al. (2002) observed an interference in their LIF-FAGE instrument during calibrations using the ozonolysis of trans-2-butene under high mixing ratios of both ozone and trans-2-butene. Tests suggested that the interference was not laser generated, and disappeared in air containing 1% water vapor. They suggested that the interference may be due to the dissociation of an intermediate in the ozonolysis mechanism that produces OH in the low-pressure cell of their FAGE instrument (Hard et al., 2002).

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Recently, Mao et al. (2012) discovered a significant interference associated with their LIF-FAGE measurements of OH in a northern California forest. Using a chemical scavenger to remove ambient OH before air enters the inlet, they found that subsequent spectral modulation revealed a significant amount of internally generated OH from an unknown interference. Measurements using only spectral modulation of the laser wavelength were greater than the measurements when the interference measured using the chemical scavenger was subtracted, and the latter measurements were in better agreement with model predictions (Mao et al., 2012). Similar results were observed by Novelli et al. (2014a) who measured ambient OH concentrations in several forest environments using an external chemical scavenger technique. They found that OH generated inside their detection cell comprised 30-80% of the daytime signal observed using spectral modulation and 60-100% of the signal observed at night. Subtracting the interference from the ambient signal resulted in OH concentrations that were in good agreement with model simulations as well as measurements by a Chemical Ionization Mass Spectrometry (CIMS) instrument (Novelli et al., 2014a).

Mao et al. (2012) found that the interference increased with both temperature and measured OH reactivity, suggesting that the interference was related to biogenic emissions in this environment, perhaps the result of BVOC oxidation products entering the sampling cell of the LIF-FAGE instrument which subsequently undergo further reactions and/or decomposition producing the additional OH signal. Novelli et al. (2016) also found that the interference appeared to correlate with temperature similar to the temperature dependence of terpene emissions and was also correlated with the measured ozone concentrations. They concluded that one possible contributor to their interference was the decomposition of stabilized Criegee intermediates inside their instrument.

In addition to decomposition leading to OH formation at ambient pressure (Fang et al., 2016; Kidwell et al., 2016; Smith et al., 2017), previous laboratory experiments have shown that BVOC ozonolysis intermediates, such as Criegee intermediates and vinyl hydroperoxides, are likely to promptly decompose to produce OH at low pressures (Kroll et al., 2001a,b). As a result of the large pressure and temperature gradients which occur as the sample enters the FAGE detection cell, the dissociation pathway of these intermediate species may be favored, leading to additional OH production. Recently, Fuchs et al. (2016) performed laboratory and chamber experiments to determine whether the ozonolysis of alkenes produced an OH artifact in their LIF-FAGE instrument. They found that under reactant concentrations that were orders of magnitude greater than ambient, the ozonolysis of propene, α-pinene, limonene, and isoprene produced a detectable interference in their instrument that increased with the turnover rate of the reaction. Extrapolating their results to ambient concentrations of ozone and alkenes would suggest that the ozonolysis of these compounds would not produce a detectable interference in their instrument under ambient conditions (Fuchs et al., 2016).

The goal of this work is to determine whether intermediates or products in the ozonolysis of various biogenic alkenes can lead to an interference with OH measurements using the Indiana University LIF-FAGE instrument (IU-FAGE). These experiments focus on the ozonolysis of several biogenic alkenes, including α-pinene, β-pinene, ocimene, isoprene, and 2-methyl-3-buten-2-ol (MBO), all of which have been observed to contribute appreciably to BVOC emissions in forested environments (Guenther et al., 1994; Harley et al., 1998). Measurements of the interference as a function of various instrumental parameters are also provided in an attempt to identify possible sources of the interference and ways it could be minimized.

2. Experimental Section

The ozonolysis experiments were performed using an atmospheric pressure turbulent flow tube with a movable injector similar to that used for ambient measurements of total OH reactivity (Hansen et al., 2014). The 1 m long and 5 cm diameter flow tube was positioned perpendicular to the IU-FAGE detection cell so that the flow would not interfere with the external OH scavenging measurement (section 2.2) (Fig. 1). A Teflon adaptor attached at one end of the flow tube supported the injector, a 1 m stainless steel tube with a 1.25 cm diameter. This injector allowed for the introduction of ozone produced from an ozone generator (Enaly) to the system and could be moved throughout the flow tube to permit varying reaction times between approximately 100 and 420 ms calculated based on the measured velocity in the flow tube. Attached to the end of the injector was a turbulizer used to increase mixing of the reagents at the start of the reaction. A flow of nitrogen of 180 SLPM created a turbulent

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flow with a Reynolds number of approximately 3750. Ozone concentrations were varied between approximately 1 and 3 ppm (2×10^{13} - 7×10^{13} molecules cm^{-3}), with most measurements occurring at ozone concentrations of 2.5, 5, and 7×10^{13} molecules cm^{-3} as the ozone generator provided the highest stability at these concentrations. Ozone concentrations in the flow tube were measured using a Teledyne Photometric Ozone Analyzer (model 400E), with an estimated uncertainty of ±0.5 ppb.

BVOC concentrations were introduced into the flow tube by bubbling N_2 through the liquid compound sending the vapor into the reactor. The concentration of the BVOC was estimated from its equilibrium vapor pressure and accounting for dilution into the main flow. Several alkene concentrations were used for each experiment, with approximate concentrations of 2×10^{11} to 4×10^{13} molecules cm^{-3} for α-pinene (Aldrich, 98%), 1×10^{11} to 4×10^{13} molecules cm^{-3} for β-pinene (Aldrich, 99%), 9×10^{10} to 5×10^{13} molecules cm^{-3} for ocimene (Aldrich, mixture of isomers, >90%), and approximately 8×10^{13} molecules cm^{-3} for isoprene (Aldrich, 99%), and MBO (Aldrich, 98%). Unfortunately, no direct method for measuring the concentration of these BVOCs was available, and as a result the absolute concentration of BVOCs in the flow tube is highly uncertain due to potential wall losses prior to entering the flow tube.

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2.1 Detection of OH Radicals

OH radicals were measured using the IU-FAGE instrument, in which ambient air is pulled through either a 0.6 or 1 mm diameter nozzle and expanded to a total pressure of approximately 4-9 Torr resulting in a total flow rate of approximately 8-10 SLPM (Dusanter et al., 2008; 2009; Griffith et al., 2013; 2016). Previous field measurements using the IU-FAGE instrument have incorporated a cylindrical inlet (5 cm diameter, 14 cm long) attached to the main detection block resulting in a total distance of approximately 20 cm from the nozzle to the detection volume (Fig. 2). These previous field measurements have utilized both the 0.6 mm nozzle (Griffith et al., 2016) and the 1 mm nozzle (Dusanter et al., 2009; Griffth et al., 2013), and the experiments presented here have attempted to reproduce these instrument configurations.

The original IU-FAGE laser system used in this study consisted of a Spectra Physics Navigator II YHP40-532Q diode-pumped Nd:YAG laser that produces approximately 5.5W of radiation at 532 nm at a repetition rate of 5 kHz. This laser pumped a Lambda Physik Scanmate 1 dye laser (Rhodamine 640, 0.25 g L^{-1} in isopropanol) that produced tunable radiation around 616 nm, which was frequency doubled to generate 2 to 20 mW of radiation at 308 nm. This laser system was recently replaced with a Spectra Physics Navigator II YHP40-532Q that produces approximately 8 W of radiation at 532 nm at a repetition rate of 10 kHz that pumps a Sirah

Credo Dye laser (255 mg/L of Rhodamine 610 and 80 mg/L of Rhodamine 101 in ethanol), resulting in 40 to 100 mW of radiation at 308 nm. Initial measurements of the OH interference from ocimene and α-pinene ozonolysis were made using the original laser system, with the majority of experiments done using the newer laser system.

After exiting the dye laser, the beam is focused onto a 12 m optical fiber to transmit the radiation to the sampling cell where it crosses the expanded air perpendicular to the flow approximately 24 times in a multipass White cell configuration (Fig. 2). The OH molecule is excited and detected using the $A^2\Sigma^+$ ($v' = 0$)←$X^2\Pi_i$ ($v'' = 0$) transition near 308 nm. A reference cell where OH is produced by thermal dissociation of water vapor is used to ensure that the laser is tuned on-line and off-line of the OH transition to measure the net fluorescence signal. The OH fluorescence is detected by a gated microchannel plate detector (Hamamatsu R5916U-52) and the resulting signal is sent through a preamplifier (Stanford Research SR445) and a photon counter (Stanford Research SRS 400). The detector is switched off during the laser pulse through the use of electronic gating, allowing the OH fluorescence to be temporally filtered from laser scatter. Each offline measurement is recorded for approximately 10 seconds and is averaged and subtracted from the online measurement, averaged for approximately 20 seconds. These measurements are recorded for at least 5 cycles per ozone concentration once the OH concentration has stabilized after several minutes.

The sensitivity of the IU LIF-FAGE instrument was calibrated using the UV-water photolysis technique where water vapor is photolyzed to produce known amounts of OH (Dusanter et al., 2008). In these experiments, calibrations were performed under the conditions of the experiments using N_2, resulting in larger calibration factors compared to ambient air due to fluorescence quenching by oxygen. Nitrogen from liquid boil-off was used instead of synthetic air to reduce the concentration of reactive impurities in the flow tube. The N_2 calibration factors were determined for various instrumental parameters including three cell pressures (4, 7, and 9 Torr), the two nozzle diameters (0.6 mm and 1 mm), and three inlet lengths (3.2 cm, 14 cm, and 24.8 cm) (Table S1, Fig. S1). For reference, previous ambient measurements using the IU LIF-FAGE instrument were typically acquired using the medium inlet length (Fig. 2) and both the 0.6 and 1 mm nozzle diameters, resulting in cell pressures of 4-7 Torr depending on the nozzle diameter size and pumping efficiency (Lew et al., 2017a). The error associated with the UV-water photolysis calibration technique is estimated to be ±36% (2σ) (Dusanter et al., 2008)

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Both nozzle diameters showed similar sensitivities that decreased as the pressure increased due to increased collisional quenching of the OH fluorescence. The calibration factor was also sensitive to the length of the inlet where the ambient air enters the cell and where the OH fluorescence occurs in the detection axis, with the sensitivity decreasing with the increasing inlet length likely due to increased loss of OH radicals on the interior walls of the inlet. For these experiments, the limit of detection was between approximately 5×10^5 - 4×10^6

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molecules cm^{-3} (S/N=1, 10 min integration) depending on the inlet configuration, flow rate, and pressure inside the FAGE detection cell, with the lowest value corresponding to the shortest inlet and lowest pressure, and the highest value corresponding to the longest inlet and highest pressure.

2.2 Measuring the OH Interference

The OH interference was measured using a chemical titration scheme in which perfluoropropylene (C_3F_6, 99.5%, Matheson) was added through a circular ring surrounding the detection inlet to chemically remove external OH (Griffith et al., 2016) (Fig. 2). Measurements of OH concentrations using spectral modulation compared to chemical modulation with C_3F_6 added externally can reveal OH radicals that are generated inside the detection cell. C_3F_6 was used because it reacts quickly with OH while also having a negligible optical absorption around 308 nm (Mao et al. 2012). The injector is approximately 3.5 cm in diameter and 1.0 cm in height and consists of 10 equally spaced 0.4 mm holes in the ring that surround the inlet nozzle at the center of the injector. The holes are approximately 0.5 cm in above the level of the detection cell inlet. Increasing the height of the injector above the inlet from 0.5 cm to 4.5 does not impact the overall sensitivity of the instrument, suggesting that OH radicals are not lost on the outer walls of the injector.

To determine the flow of C_3F_6 to be used, OH was produced from the photolysis of ambient air using a mercury penlamp placed in front of the inlet (Fig. S2). Once a constant OH signal was established, C_3F_6 was added at varying flows to determine the flow that depleted ≥90% of the external OH signal (a total flow of 99.5% C_3F_6 of approximately 3-5 sccm). With the flow entering the detection cell inlet of 3-9 SLPM depending on inlet diameter size, this flow of C_3F_6 results in an approximate concentration of 1-3 × 10^{16} molecules cm^{-3} and a residence time of approximately 0.05 s. This flow rate was able to titrate the externally generated OH regardless of the flow rate set by each individual inlet diameter. To ensure that this flow of C_3F_6 did not titrate OH radicals produced inside the detection cell, a penlamp was placed inside the detection cell directly behind the inlet to generate OH radicals internally. The same external C_3F_6 flow was again introduced to ensure that the concentration of C_3F_6 after expansion into the detection cell was not high enough to titrate any internally generated OH.

By applying this C_3F_6 titration method to the alkene ozonolysis experiments, any OH produced in the flow tube was expected to be removed. Although the ozonolysis reactions may still lead to additional OH production during the residence time in the injector, kinetic simulations suggest that under the conditions of these experiments the steady-state concentration of OH in the presence of C_3F_6 would be near or below the detection limit of the instrument (less than 5 × 10^5 molecules cm^{-3}). However, for some of the high concentration experiments, the amount of C_3F_6 added may not have been sufficient to reduce the steady-state concentration of

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Moved up [1]: Measurements of OH concentrations using spectral modulation with C_3F_6 added externally reflect OH radicals generated inside the detection cell. C_3F_6 was used because it reacts quickly with OH while also having a negligible optical absorption around 308 nm (Mao et al. 2012).

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OH to below the detection limit of the instrument, especially for the ocimene experiments due to the high reactivity of ocimene with ozone. However, the model simulations suggest that even for these high concentration experiments the remaining steady-state OH concentrations represented less than 10% of the observed interference. Thus, the majority of OH that was measured using spectral modulation after C_3F_6 addition would be an interference generated internally. Subtraction of this interference from the measurement acquired before C_3F_6 addition should reflect the steady-state OH concentration generated in the flow tube, which can then be compared to literature values of the OH yield for the ozonolysis of these alkenes.

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3. Results and Discussion

3.1 Ozonolysis experiments

The interference tests were performed during the alkene ozonolysis experiments with a reaction time in the flow tube of approximately 420 ms, a reaction time longer than that required for the system to reach steady-state (less than approximately 20 ms based on model calculations), and the results are shown in Figs. 3 and 4. In these figures, the open symbols are the measured OH concentration produced from the ozonolysis reaction without addition of C_3F_6 (With interference), and the filled symbols represent the OH signal after the signal measured with C_3F_6 addition is removed (Without interference) using the 0.6 mm nozzle, shown on the same plot to illustrate the magnitude of the interference. The expected steady-state OH concentrations based on previous measurements of the OH yield for each compound are also shown in each figure by the solid line, calculated using the following equation:

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$$[\mathrm{OH}]_{ss} = \frac{k_{O_3+VOC}\alpha[O_3][alkene]}{k_{OH+VOC}[alkene] + k_{OH+O_3}[O_3] + k_{wall}} \approx \frac{k_{O_3+VOC}\alpha[O_3]}{k_{OH+VOC}} \quad (1)$$

In this equation, k_{O3+VOC} is the rate constant for the O_3 + alkene reaction with an OH yield of α, k_{OH+VOC} is the rate constant for the OH + alkene reaction, k_{OH+O3} is the rate constant for the OH + O_3 reaction, and k_{wall} is the first-order loss of OH on the walls of the reactor, measured as described in Hansen et al. (2014). Determining the expected steady-state OH concentration from this equation has the advantage of being independent of the concentration of each BVOC. Rate constants for the OH and O_3 reactions were obtained from recommendations by Atkinson (1997) and Atkinson et al. (2006). For these calculations, the loss of OH from reaction with ozone (approximately 7 s^{-1}) as well as wall loss of OH (approximately 3.6 s^{-1}), were neglected, as they were much smaller than loss of OH due to reaction with the alkenes due to the high concentration of alkenes used in these experiments.

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As illustrated in Fig. 3, the measured OH concentration from the ozonolysis of α-pinene without C_3F_6 addition is consistently greater than the measurements after the interference is subtracted, indicating that a significant concentration of OH is being produced inside the detection cell. In these figures, instabilities in the concentration of ozone produced by the ozone generator resulted in small variations in the measured ozone concentrations between measurements with and without added C_3F_6. Experiments without α-pinene in which ozone alone was sampled by the detection cell showed a negligible OH signal, suggesting that the interference was related to the presence of both the alkene and ozone. The observed interference measured with the addition of C_3F_6 accounted for approximately 40-60% of the observed signal in the absence of C_3F_6. When the measured interference was subtracted from the overall signal, the resulting OH concentrations were in reasonable agreement with the OH yield expected from α-pinene ozonolysis resulting in an OH yield of approximately 0.81 ± 0.10, determined from a weighted fit of the slope of the plot of the OH concentration versus ozone concentration, in good agreement with the value of 0.76 ± 0.11 as reported by Chew and Atkinson (1996) and the value of 0.91 ± 0.23 reported by Siese et al. (2001).

The measured interference appeared to depend on the length of the inlet, with the greatest interference observed with the longest inlet (Fig. 3), while the interference measured with the short and medium length inlets were comparable. Similar results were observed with the use of the 1 mm nozzle diameter (Fig. S3), with the longest inlet displaying the greatest interference. These results are similar to that observed by Fuchs et al. (2016), who found that the interference from the ozonolysis of α-pinene, limonene and isoprene also increased with the length of the inlet in their FAGE instrument. But while the inlet length appears to exhibit a trend in the OH interference, the cell pressure did not appear to significantly impact the level of the interference except at the longest inlet length. These results are in contrast to the results of Fuchs et al. (2016), who found that the interference in their instrument decreased with cell pressure, although the effect was greater with the longer inlet. The different cell pressures in these experiments were obtained by changing the pumping speed, which impacts the velocity and residence time of the airstream inside the detection cell. This suggests that increasing the reaction time for the short and medium length inlets does not significantly impact the interference, while increasing the reaction time for the longest inlet does increase the interference. However, at the longest inlet length, the increased reaction time likely also leads to increased collisions with the interior surfaces of the detection cell, which could also lead to increased dissociation and production of OH. Increasing the nozzle diameter decreases the flow velocity inside the detection cell, which increases the reaction time and the frequency of wall collisions using the longer inlet length. Although this also increases the loss of OH generated by the interference, it appears that the rate of production of OH by the interference is greater than the loss rate of OH on the walls of the inlet. These

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results appear to be independent of the α-pinene concentration (Fig. 4, top) as the level of the interference is similar for estimated α-pinene concentrations between approximately 1 and 4×10^{13} molecules cm^{-3}.

The results from the ozonolysis of β-pinene are also shown in Fig. 4 (middle). Similar to that observed for the ozonolysis of α-pinene, the observed interference measured with the addition of C_3F_6 accounted for approximately 40% of the observed signal in the absence of C_3F_6. When the measured interference was subtracted from the overall signal, the measured OH concentrations results in an overall OH yield of approximately 0.40 ± 0.01, which is in good agreement with the value reported by Atkinson et al. (1992) of 0.35 ± 0.05. The percentage of interference as well as the resulting OH yield was relatively constant for each β-pinene concentration used; however, the results suggest that the OH yield may increase with increasing concentrations of β-pinene.

Measurements of the concentration of OH produced from the ozonolysis of various concentrations of ocimene are also shown in Fig. 4 (bottom). In contrast to the ozonolysis of α-pinene, the interference and the observed OH yield appear to increase with increasing ocimene concentration. At ocimene concentrations of approximately 4×10^{11} molecules cm^{-3}, an OH yield of approximately 0.28 ± 0.02 was measured. However, the apparent OH yield increased to a yield of 1.0 ± 0.03 at the highest ocimene concentration (approximately 5×10^{13} molecules cm^{-3}). Additional ocimene ozonolysis experiments were performed using the two nozzle diameters and three inlet lengths with the results shown in Fig. S4. These results show that the measured OH yield from ocimene ozonolysis after subtracting the interference is only consistent with the results of Aschmann et al. (2002) of 0.55 ± 0.09 for an ocimene concentration of approximately 1×10^{13} molecules cm^{-3}. The increase in the apparent OH yield and interference as the concentration of ocimene was increased may be due to the additional ozonolysis of the reaction products, as the products of ocimene ozonolysis are unsaturated. The higher ocimene concentrations would lead to increased concentrations of reaction products, which in turn could also contribute to the measured interference and OH yield. Additional experiments are needed in order to better quantify the OH yield from the ozonolysis of ocimene.

In contrast to the measurements involving α-pinene, β-pinene, and ocimene, similar ozonolysis experiments involving isoprene and MBO did not produce a detectable OH signal or interference under the highest ozone and alkene concentrations. These results may reflect the lower relative reactivity of isoprene and MBO with O_3 compared to reaction with OH as well as a lower yield of OH under the conditions of these experiments. Simulations of the kinetics using the MCM mechanism for the ozonolysis of isoprene result in steady-state OH concentrations that are a factor of 50 lower than that predicted for the ozonolysis of α-pinene, consistent with a lower steady-state OH concentration estimated using Equation 1, and are near or below the detection limit of the

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instrument. However, these results do not rule out the possibility of an interference from the ozonolysis of these compounds. The lower reactivity of isoprene and MBO with ozone would likely require longer reaction times or higher concentrations of ozone and/or alkenes to establish steady-state OH concentrations above the detection limit of the instrument in these experiments. Fuchs et al. (2016) did find a significant unexpected OH signal in laboratory under very high concentrations of isoprene and a reaction time on the order of 1 s. Future experiments will involve higher concentrations of ozone, isoprene and MBO and/or longer reaction times to increase the ozonolysis rate for these reactions and to determine the potential magnitude of the interference from isoprene and MBO in the IU-FAGE instrument.

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3.2 Interference measurements as a function of laser power, ozone, and ozonolysis reaction time

A potential interference with the detection of OH radicals by laser-induced fluorescence is the production of OH through photolysis of ozone by the laser, with the resulting excited oxygen atoms reacting with ambient water vapor to produce OH (reactions R1 and R2) (Stevens et al., 1994; Ren et al., 2004):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow OH + OH \quad \text{(R2)}$$

The resulting OH signal from this two-photon process would display a quadratic dependence on laser power. One possible source of the interference observed in the ozonolysis experiments could be $O(^1D)$ produced from the photolysis of ozone by the laser reacting with the alkene leading to the production of OH radicals through a hydrogen abstraction mechanism. The OH signal from this two-photon process would also display a quadratic dependence on laser power.

To confirm that laser generated OH was not occurring within this instrument and was not the source of the interference, experiments were conducted over a wide range of laser powers (0.6-12 mW) to determine whether the observed interference displayed a dependence on laser power consistent with a laser-generated mechanism. Fig. 5 (top) shows the measurements of the OH concentration with and without the interference for the ozonolysis of ocimene as a function of laser power. These experiments were done under dry conditions to minimize potential laser-generated interferences from reactions R1 and R2. Because the OH concentration remained relatively stable over the range of laser powers used in these experiments, there is no indication that the interference was due to a laser-generated mechanism. These results are similar to that found by Novelli et al. (2014a) and Fuchs et al. (2016).

A plot of the interference at different ozone concentrations is also shown in Fig. 5 (middle) for the ozonolysis of α-pinene as an example. Comparing the measured interference for each inlet length and ozone

concentration shows a trend in which the interference appears to increase with increasing ozone concentration, with the greatest increase occurring with the longest inlet. Similar to the results of Fuchs et al. (2016), the observed interference appears to increase with the overall ozonolysis turnover time, defined as the steady-state rate of OH radical propagation, expressed here as the rate of alkene ozonolysis (Fig. 6). Although the magnitude of the interference observed here is greater due to the greater turnover rates used in these experiments, the slope of the observed interference using the short inlet as a function of the turnover rate appears to be similar to that observed by Fuchs et al. (2016), although the results presented here are highly scattered, likely due to the large uncertainty associated with estimating the concentration of each BVOC. However, the level of the observed interference is greater than that illustrated in Fig. 6 for the measurements using the long inlet, suggesting the similarity with the results of Fuchs et al. (2016) may be fortuitous, as differences in the design of the instrument impacts the level of the interference. In contrast to the results of Fuchs et al. (2016), the level of interference as a function of the turnover rate is not similar for all of the BVOCs tested. While the observed interference as a function of turnover rate appears to be similar for the ozonolysis of α-pinene and ocimene, the observed interference for the ozonolysis of β-pinene is significantly less. This may also be related to uncertainties associated with estimates of the concentration of β-pinene in the flow tube, but may also suggest differences in the mechanism for the production of the interference for some BVOCs. Additional measurements of the interference for other BVOCs are needed to resolve this discrepancy.

The interference signals from the ozonolysis of α-pinene, β-pinene, and ocimene for each experimental condition are summarized in Table S2. The interference from α-pinene expressed as a percentage of the total OH signal at several ozone concentrations and cell pressures for the short, medium, and long inlets are shown in Fig. S5. On average, the percent interference was similar for ozone mixing ratios between 1-3 ppm, with values of approximately 45 ± 3%, 37 ± 8%, and 58 ± 8% for the short, medium, and long inlets, respectively for the 1 mm nozzle, and approximately 54 ± 7%, 50 ± 13%, and 65 ± 11% for the short, medium, and long inlets, respectively for the 0.6 mm nozzle. As discussed above, the similarity of the measured interference between the short and medium length inlets suggest that the level of interference is not directly related to the residence time inside the FAGE detection cell, but may be the result of increased collisions with the interior surfaces of the detection cell that occurs when using the longest inlet. Similar results were observed for the ozonolysis of ocimene (Fig. S6), although additional experiments will be needed to determine whether a similar trend with inlet length and residence time is observed.

The interference was also measured over varying reaction times within the flow tube, and an example of the results is shown in Fig. 5 (bottom). The results appear to indicate that the level of interference does not depend

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on the ozonolysis reaction time in the flow tube. If the interference was due to a stable oxidation product, it would be expected to increase with reaction time as the concentration stable oxidation products accumulated in the flow tube. These results suggest that the interference is not due to a stable oxidation product but may instead be due to a steady-state intermediate in the ozonolysis mechanism. The consistency of the measured interference relative to the OH concentration produced from the ozonolysis mechanism may suggest that the source of the interference is related to the source of OH, such as the Criegee intermediate.

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3.3 Stabilized Criegee intermediates as a source of the interference

3.3.1 Decomposition of Criegee intermediates produced inside the FAGE detection cell as a source of the interference. The ozonolysis of alkenes involves the addition of ozone to the double bond, forming a primary ozonide which quickly decomposes to an excited Criegee intermediate and a carbonyl compound. Depending on its structure, the excited Criegee intermediate can either decompose to form an OH radical, or can be stabilized by collisions forming a stabilized Criegee intermediate (SCI), which can also thermally dissociate into OH at longer reaction times (approximately 1 sec for tetramethylethylene, Kroll et al., 2001b). At shorter reaction times, the excited Criegee intermediate is in steady-state with respect to dissociation and stabilization, resulting in OH concentrations that are generally independent of reaction time, but increase at longer reaction times due to the additional OH production from SCIs (Kroll et al., 2001b). Rate constants for decomposition and stabilization of excited Criegee intermediates are estimated to be on the order of 10^4-10^9 s^{-1} (Horie and Moortgat, 1991), while the rate constant for decomposition of stabilized Criegee intermediates have been measured to be on the order of 10^2 s^{-1} (Smith et al., 2016). As a result, the concentration of excited Criegee intermediates are expected to be very low compared to the concentration of SCIs, which have estimated lifetimes on the order of milliseconds relative to decomposition. The atmospheric fate of SCIs will depend on the rate of decomposition relative to reaction with other atmospheric trace gases such as SO_2 or H_2O among others (Novelli et al., 2014b). This lifetime may be longer in the low pressure region of the FAGE detection cell due to the decrease in concentration of reactants such as SO_2 or H_2O, allowing these SCIs to collide with the walls of the detection cell.

The time dependence of the observed interference in these experiments, with the interference appearing to be independent of reaction time except under the longest reaction time, at first appears be consistent with a mechanism that involves the formation of excited Criegee radicals inside the FAGE detection cell. However, it is unlikely that excited Criegee intermediates could be produced directly from alkene ozonolysis inside the IU-FAGE detection cell as the decrease in reactant concentrations from the expansion to low pressure leads to turnover rates that are approximately two orders of magnitude smaller than that shown in Fig. 6. For the ozonolysis

of α-pinene, a reaction time of approximately 0.5-1 s would be required to internally produce the observed OH signals in these experiments, which is much longer than the reaction time inside the detection cell (on the order of 1-2 ms). The short reaction time in the detection cell is also too short for OH concentrations to reach steady-state. The lower pressure in the FAGE detection cell may result in higher yields of OH due to the lower rate of stabilization of the excited Criegee intermediate under these conditions (Kroll et al., 2001a). Nevertheless, an OH yield of one would still require a reaction time of approximately 0.18 to 0.35 s to produce the observed internal OH concentrations.

3.3.2 Decomposition of Criegee intermediates produced outside of the FAGE detection cell as a source of the interference. Previous measurements have demonstrated that the stabilized Criegee intermediates produced external to the FAGE detection cell from the ozonolysis of propene and (*E*)-2-butene can decompose to produce OH radicals upon entering the low pressure region of the FAGE detection cell (Novelli et al., 2014b). The time dependence of the OH production was consistent with previous measurements of the rate of unimolecular decomposition of SCIs (Novelli et al., 2014b). To determine whether the decomposition of stabilized Criegee intermediates are the source of the interference in these experiments, acetic acid was added to the flow tube as an SCI scavenger. Welz et al. (2014) have reported direct measurements of the rate constants for the reactions of CH_2OO and CH_3CHOO Criegee intermediates with formic and acetic acids and found values in excess of 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. In contrast, the rate constant for reaction of acetic acid with OH is approximately 7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006). Acetic acid was chosen over SO_2 or water as an SCI scavenger as SO_2 fluorescence at 308 nm can interfere with OH measurements (Fuchs et al., 2016), while the addition of water in the presence of the high concentrations of ozone in these experiments would have led to significant laser-generated OH from reactions R1 and R2. Assuming that other Criegee intermediates react similarly, addition of acetic acid should scavenge SCIs in the flow tube. If SCIs are the source of the OH interference, the measured OH signal resulting from addition of acetic acid should be equivalent to the OH signal when the OH interference measured using external C_3F_6 titration is subtracted. For these experiments, approximately 9×10^{12} molecules cm^3 of acetic acid was introduced into the flow tube, and allowed to react for approximately 200 ms. At this concentration, the reaction with acetic acid was modeled to have a minimal impact on the steady-state concentration of OH.

The results of these experiments for the ozonolysis of α-pinene and ocimene are shown in Fig. 7. In this figure, the open symbols are the measured total OH signal due to OH produced in the flow tube from both excited and stabilized Criegee intermediates plus the OH interference, while the solid red symbols represent the remaining OH signal after the interference (measured after external C_3F_6 addition) is subtracted. The solid green symbols represent the measured OH signal (without external C_3F_6 addition) when acetic acid is added to the flow tube. As

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can be seen from this figure, the measured OH signal when acetic acid is added is similar to the OH signal when the interference is subtracted, suggesting that the interference is due to the decomposition of SCIs inside the IU-FAGE detection cell, consistent with the results of Novelli et al. (2014b). These results also suggest that the majority of the OH radicals in the flow tube are produced from the rapid decomposition of excited Criegee radicals. If stabilized Criegee intermediates were responsible for a significant fraction of the OH produced in the flow tube, it is likely that addition of acetic acid would have led to measured OH signals that were significantly lower than the OH signal after the interference was subtracted. However, these results do not exclude the possibility that SCIs are also thermally decomposing and contributing to OH production in the flow tube. Recent measurements suggest that the unimolecular decomposition of the $(CH_3)_2COO$ Criegee intermediate can be rapid and compete with reaction of this intermediate with water or SO_2 (Smith et al., 2016; Chhantyal-Pun et al., 2017). A similar rate for the decomposition of SCIs in the experiments reported here could also compete with reaction of this intermediate with acetic acid. Additional experiments are needed to determine whether stabilized Criegee intermediates contribute to OH radical production in the ozonolysis mechanisms of these biogenic compounds.

To determine whether the magnitude of the interference observed in these experiments was consistent with the concentration of stabilized Criegee intermediates in the flow tube, the concentration of these intermediates was estimated from a chemical model of the ozonolysis of α-pinene using the Master Chemical Mechanism (MCM v3.2, Jenkin et al., 1997; Saunders et al., 2003). In this mechanism, the ozonlysis of α-pinene results in the formation of two Criegee intermediates, APINOOA and APINOOB. APINOOA decomposes to OH radicals through two channels with different co-products with a decomposition rate constant of 1×10^6 s^{-1}. APINOOB also decomposes to form an OH radical with a decomposition rate constant of 0.5×10^6 s^{-1}, but can also form a stabilized Criegee intermediate (APINBOO) with a rate constant of 0.5×10^6 s^{-1}. In addition to reaction with CO, NO, NO_2, and SO_2 (which are not significant in these experiments), the stabilized Criegee intermediate in this mechanism can also decompose to form pinonaldehyde or pinonic acid, with rate constants that depend on the concentration of water vapor ($1.40 \times 10^{-17} * H_2O$ and $2.00 \times 10^{-18} * H_2O$ s^{-1}, respectively). This version of the MCM does not include a mechanism for the formation of OH from the stabilized Criegee intermediate, nor does it distinguish between the *syn* and *anti* isomers of the Criegee intermediates, which may have different decomposition rates and yields. Despite its potential shortcomings, the mechanism was used for simplicity to provide a rough estimate of the concentration of Criegee intermediates to compare with the experimental measurements.

Under the conditions of these experiments, the model predicts a steady-state concentration of stabilized Criegee intermediates (APINBOO) of approximately 2-6 × 10^8 molecules cm^{-3} (Fig. 7). Based on these results,

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the observed OH interference in these experiments could be explained if approximately 5% of these intermediates dissociated and produced OH radicals inside the IU-FAGE detection cell, assuming that the transmission of these stabilized Criegee intermediates through the inlet is similar to that for OH. In contrast, the MCM predicted steady-state concentration of excited Criegee radicals (APINOOA and APINOOB) in the flow tube was calculated to be on the order of 10^3 molecules cm^{-3}, much less than the observed interference. Thus it is unlikely that excited Criegee intermediates are the source of the interference, but rather the interference is the result of decomposition of SCIs in the FAGE detection cell. These results are in contrast to the results of Fuchs et al. (2016), who found that in their ozonolysis experiments that the addition of SO_2 as a scavenger for Criegee intermediates did not affect the observed OH signal. They concluded that SCIs were not the cause of the interference in their instrument, although they could not rule out that the interference was due to the decomposition of particular SCI isomers that did not react with SO_2 (Fuchs et al., 2016).

If stabilized Criegee intermediates are the source of the interference in these measurements, one might have expected to observe an interference associated with the ozonolysis of isoprene even though the expected yield of OH was below the detection limit of the instrument. Simulations using the Master Chemical Mechanism suggest that the concentration of SCIs in the isoprene ozonolysis mechanism are similar to the concentration of SCIs in the α-pinene ozonolysis mechanism. Given that OH yield from the decomposition of excited CIs in the isoprene mechanism is lower than that for the α-pinene mechanism, the absence of a detectable interference in the isoprene experiments described here may suggest that the decomposition of these intermediates inside the FAGE detection cell may also be slower. Consistent with the observation that the observed interference appears to be a constant fraction of the total OH yield in these experiments independent of the ozone concentration and the turnover rate (Figs. S5 and S6), the observed interference for each alkene is likely proportional to the OH yield from the ozonolysis mechanism, with the absence of an observed interference in the isoprene experiments consistent with the lower OH yield in the isoprene ozonolysis mechanism. Additional experiments measuring the interference from the ozonolysis of isoprene is needed to resolve this issue.

3.3.3 Interference from Criegee intermediate decomposition on LIF-FAGE calibrations. These results also imply that using the ozonolysis of alkenes as a potential source for calibrating LIF-FAGE instruments may lead to an overestimation of the instrument sensitivity given the potential for this source to produce an interference. As mentioned above, Hard et al. (2002) observed an interference in their LIF-FAGE instrument during calibrations using the ozonolysis of trans-2-butene under high mixing ratios of both ozone (up to 28 ppm) and trans-2-butene (greater than 12 ppb). They found that the interference disappeared in the presence of 1% water vapor. Given the potentially rapid reaction of Criegee intermediates with water vapor (Chao et al., 2015), this may suggest that the

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source of their interference was also the decomposition of Criegee intermediates inside their detection cell. However, Dusanter et al. (2008) found that the instrument sensitivities derived from the ozone-alkene calibration technique using trans-2-butene were systematically lower than those derived from the water-vapor UV- photolysis technique, in contrast to what might be expected if the measurements from the ozonolysis technique were impacted by an interference from Criegee intermediates. But because these ozonolysis experiments were done under humid conditions, it is possible that the Criegee intermediates were scavenged by water vapor prior to entering the IU-FAGE detection cell, thus minimizing the interference. Although the rate constant of Criegee intermediates with water vapor depends on the structure of the intermediate (Vereecken et al., 2015), future calibrations of LIF-FAGE instruments using the ozonolysis of alkenes should be done in the presence of water vapor or another Criegee scavenger to insure that the calibration is not influenced by this potential interference.

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4. Atmospheric Implications

The percent interference observed in these studies (Figs. S5, S6) is similar to the ambient measurements reported by Mao et al. (2012), who measured an interference that was approximately 50% of the total OH signal in an environment dominated by 2-methyl-3-buten-2-ol (MBO), monoterpenes, sesquiterpenes, and related oxygenated compounds. Novelli et al. (2014a) also found that in their measurements of OH in several forest environments the interference accounted for 30-80% of their total OH signal during the daytime. External addition of SO_2 as an SCI scavenger during some of these measurements resulted in the complete removal of the interference, suggesting that the source of the interference was the decomposition of ambient SCIs inside their detection cell (Novelli et al., 2016). However, the magnitude of the interference signal relative to the calibration for OH was much greater than the expected concentration of SCIs in these environments, which was estimated to be on the order of 5×10^4 molecules cm^{-3} (Novelli et al., 2016). One possible reason for this discrepancy is a greater sensitivity of the LIF-FAGE instrument to the detection of ambient SCIs relative to ambient OH, perhaps due to a greater transmission efficiency of SCIs into the FAGE detection cell. Tests to measure the sensitivity of their LIF-FAGE instrument to the detection of SCIs relative to OH found that the transmission of *syn*-CH_3CHOO through different nozzle designs was different from the transmission of OH radicals (Novelli et al., 2016). These results suggest that the sensitivity of their LIF-FAGE instrument may be different for the detection of SCIs and that using the calibration factor for OH radicals to estimate the SCI concentration from the interference may not be appropriate. However, the sensitivity of their LIF-FAGE instrument to detection of SCIs would have to be a factor of 100 greater than that for OH based on the estimated concentration of ambient SCIs (Novelli et al., 2016). Previous measurements

on a similar LIF-FAGE instrument demonstrated that the measured OH signal is relatively insensitive to the shape and coating of the inlet (Stevens et al., 1994). In addition, external calibrations including inlet losses were found to be similar to internal calibrations that did not use the inlet. These results imply that heterogeneous loss of OH radicals on the inlet is not occurring to a significant extent (Stevens et al., 1994).

Similar to that observed by Fuchs et al. (2016), extrapolating the interference observed in the experiments presented here as a function of the ozonolysis turnover time (Fig. 6) to concentrations and turnover rates typically observed in the atmosphere (approximately 1.5 ppb hr^{-1}, Hakola et al., 2012; Fuchs et al., 2016) would suggest that the interference under ambient conditions would be near the detection limit of the IU-FAGE instrument (approximately 4×10^5 molecules cm^{-3}). Consistent with this result, previous measurements of OH radical concentrations by the IU-FAGE instrument in an urban environment during CalNex (California Research at the Nexus of Air Quality and Climate Change) using the external chemical titration technique found no evidence of an unknown interference (Griffith et al., 2016). Measurements of OH by the IU-FAGE instrument in a forested environment in northern Michigan during and after the CABINEX (Community Atmosphere-Biosphere Interactions Experiment) campaign using the external chemical titration technique also did not reveal any unknown interferences (Griffith et al., 2013). However, the measurements during CABINEX were done under relatively cool conditions and low ozone concentrations, where daytime maximum ozone mixing ratios were approximately 30 ppb on average. The relatively cool conditions suggest that mixing ratios of BVOCs may have been relatively low during this campaign, as mixing ratios of isoprene were less than 2 ppb. During CalNex, maximum daytime mixing ratios of ozone were higher (approximately 50-60 ppb on average during the week and approximately 70-80 ppb on average on the weekends), but mixing ratios of isoprene were even lower, less than 1 ppb on average, (Griffith et al., 2016), suggesting that the mixing ratio of other BVOCs may also have been lower.

In contrast, recent measurements of OH concentrations by the IU-FAGE instrument in an Indiana forest using the external chemical titration technique did reveal an interference that correlated with both temperature and ozone concentrations, similar to the results of Mao et al. (2012) (Lew et al., 2017b). Compared to the conditions during CABINEX, these measurements were done under higher daytime maximum ozone mixing ratios (approximately 40 ppb) and relatively warmer conditions, where isoprene mixing ratios greater than 4 ppb suggest higher mixing ratios of other BVOCs. The magnitude of the observed interference (on the order of 10^6 molecules cm^{-3}) was similar to that observed previously by other LIF-FAGE instruments (Mao et al., 2012; Novelli et al., 2014a; 2016), and accounted for approximately 60% of the total measured OH signal on average. The known interference from laser-generated OH varied with laser power, ambient ozone and water concentrations, but was

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approximately half of the total measured interference on some days, while on other days accounted for all of the measured interference. However, similar to that observed by Novelli et al. (2016), estimates of the ambient concentration of SCIs on the order of approximately 4-5×10^4 molecules cm^{-3} for similar environments (Percival et al., 2013; Novelli et al., 2016) suggest that the observed interference in these measurements may not be solely due to ambient SCIs unless there are other significant sources of Criegee radicals that are not accounted for in these models.

These results suggest that although SCIs may be contributing to the observed interference, there may exist an unknown interference in these measurements that also correlates with the concentration of ozone and BVOCs, perhaps due to oxidation products of BVOCs not tested in the experiments reported here (Novelli et al., 2016; Fuchs et al., 2016). Recently, Fuchs et al. (2016) reported an interference in their LIF-FAGE instrument associated with NO_3 radicals, although the exact mechanism of the interference remains unknown. These results suggest that there may be other potential interferences associated with the technique in addition to the decomposition of SCIs that involve complex homogeneous and/or heterogeneous mechanisms inside the FAGE detection cell.

5. Summary and Conclusions

Measurements of OH concentrations produced from the ozonolysis of α-pinene, β-pinene, and ocimene revealed a potential interference associated with the Indiana University LIF-FAGE instrument. The observed interference did not appear to be laser generated and was independent of the ozonolysis reaction time. Addition of acetic acid resulted in measured OH concentrations that were similar to measurements when the interference was subtracted, suggesting that the source of the interference in these experiments involved the decomposition of stabilized Criegee intermediates inside the IU-FAGE detection cell. Further measurements and modeling will be needed for a wider variety of alkenes in order to confirm these results.

The interference appeared to increase with the length of the inlet in the low pressure region of the detection cell, suggesting that the interference depends on the reaction time in the detection cell. However, increasing the pressure in the detection cell by decreasing the flow rate did not significantly increase the observed interference except for the longest inlet. This may suggest that the increase in the observed interference with the length of the inlet may be the result of increased collisions of the stabilized Criegee intermediates inside the detection cell leading to the formation of OH rather than the result of an increase in reaction time. Additional experiments will be needed to confirm these results. To minimize this interference and other unknown

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interferences, future measurements of OH by the IU-FAGE instrument will test different detection cell designs to minimize any observed ambient interferences though changes in both reaction time and potential surface collisions, while also maintaining the quality of the ambient OH measurement.

Regardless, future ambient measurements by the IU-FAGE instrument will incorporate the external OH titration technique to quantify these and other potential unknown interferences. Because of differences in design (geometry, cell pressure, flow, etc.) these interference measurements may not apply to other LIF-FAGE instruments. However, it is recommended that future OH measurements using the LIF-FAGE technique incorporate an external OH titration scheme or some other method to quantify potential artefacts.

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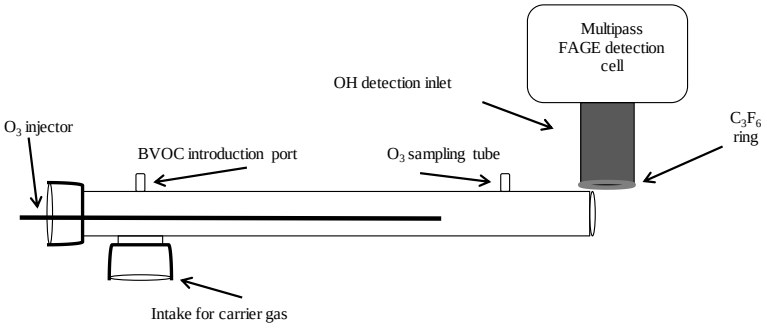

Figure 1: Schematic of the atmospheric pressure flow system used in this study.

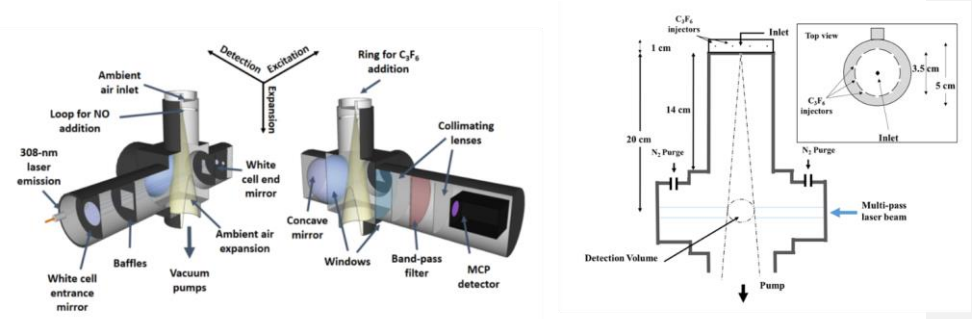

Figure 2. Schematic of the IU-FAGE sampling/excitation axis (left) and cross section with dimensions for the medium inlet configuration (right).

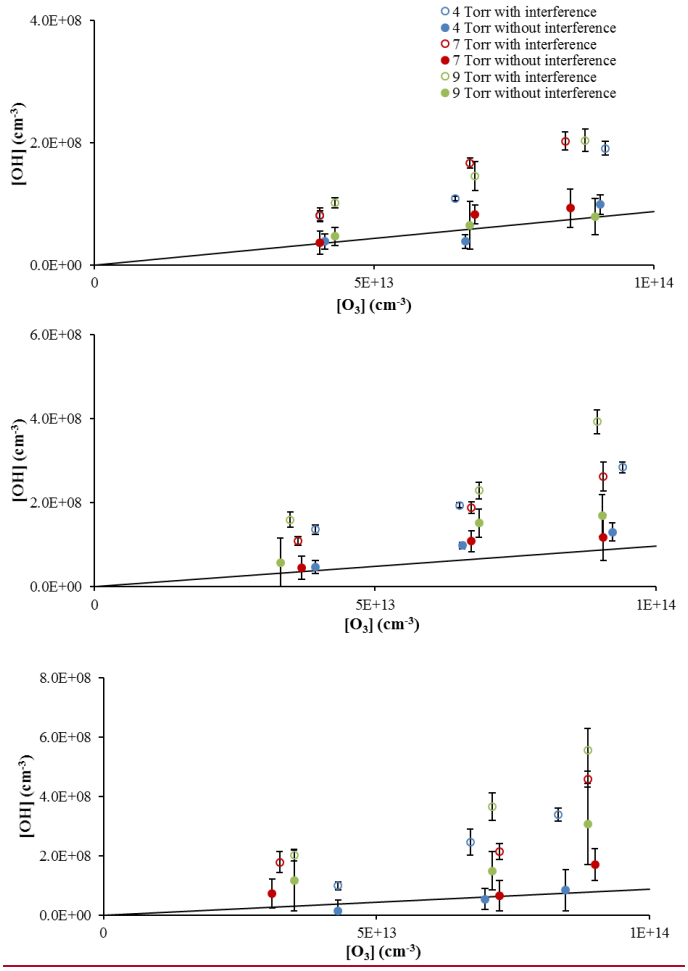

Figure 3. OH concentrations from α-pinene ozonolysis at three cell pressures with and without the interference using the 0.6 mm diameter nozzle and the short (top), medium (middle), and long (bottom) inlet lengths with α-pinene concentrations of approximately 3×10^{12} cm^{-3}. Error bars indicate the precision of the measurement (1σ). Lines indicate the expected steady-state OH concentration based on published values of the OH yield (see text).

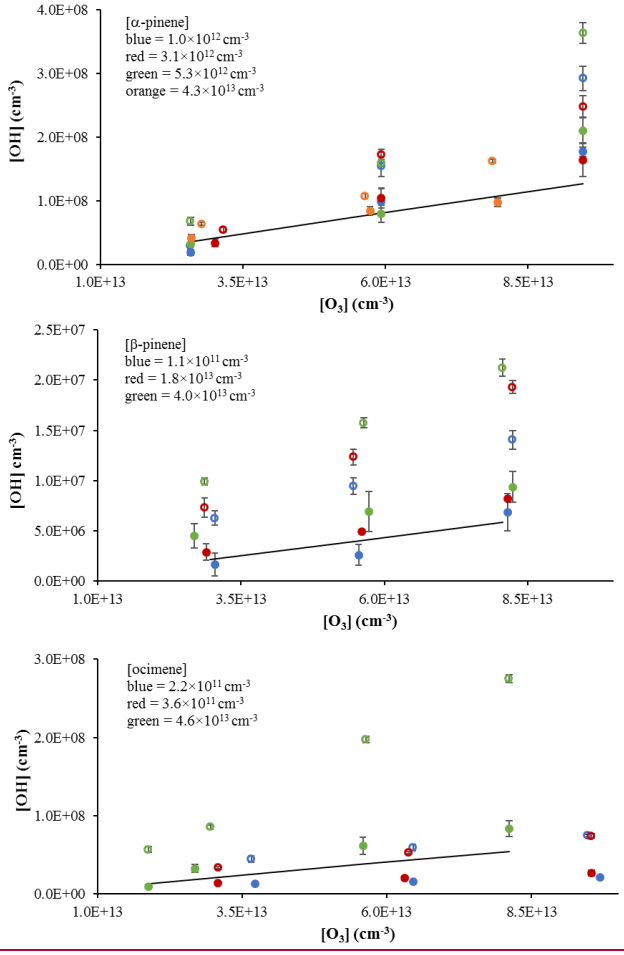

Figure 4. OH concentrations using the short inlet from the ozonolysis of α-pinene (top), β-pinene (middle), and ocimene (bottom). Open circles indicate measurements with the interference, filled circles indicate measurements without the interference. Colors indicate estimated concentrations. Solid lines reflect the expected OH radical yield (see text). Error bars reflect the measurement precision (1σ).

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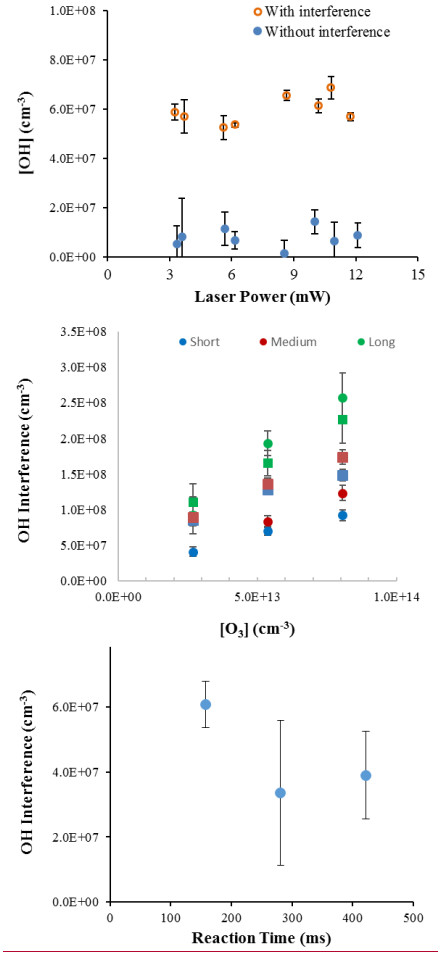

Figure 5. OH concentrations from ocimene ozonolysis with varied laser power at an ozone mixing ratio of 2 ppm and ocimene concentration of approximately 3×10^{13} cm^{-3} (top). OH interference during α-pinene (approximately 3×10^{12} cm^{-3}, circles) and ocimene (approximately 3×10^{13} cm^{-3}, squares) ozonolysis based on ozone concentration and inlet length (middle). OH interference measurements during ocimene ozonolysis as a function of reaction time with an ocimene concentration of approximately 3×10^{13} cm^{-3} (bottom).

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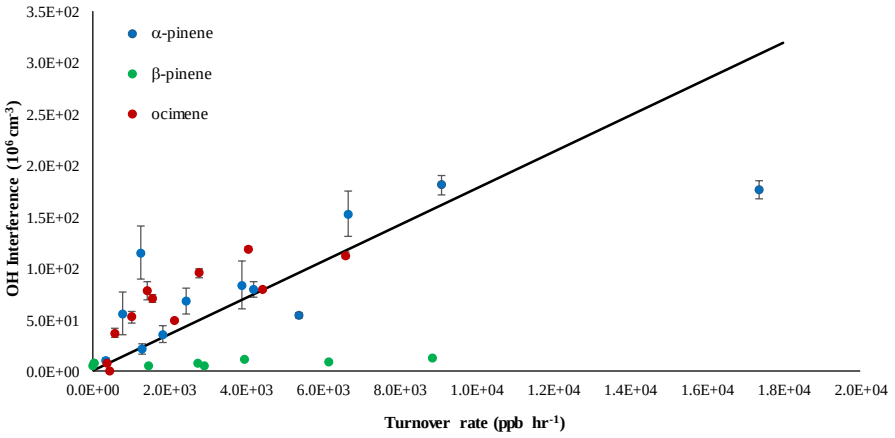

Figure 6. Interference signal as a function of turnover rate for the ozonolysis of α-pinene, β-pinene, and ocimene using the short inlet. Solid line reflects the slope observed by Fuchs et al. (2016).

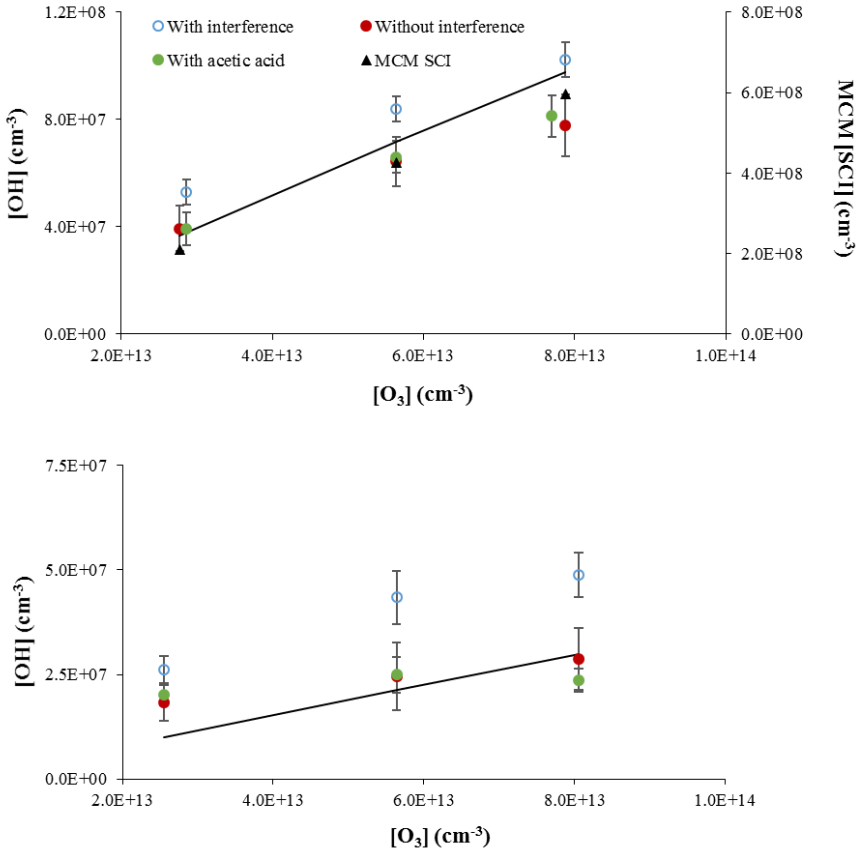

Figure 7. Measurements of OH concentrations from the ozonolysis of α-pinene (approximately 1×10^{12} cm^{-3}, top) and ocimene (approximately 4×10^{11} cm^{-3}, bottom). Open symbols are measurements including the interference, filled red circles are the resulting OH measurements when the interference determined by C_3F_6 addition is subtracted, and the filled green circles are the OH measurements when acetic acid is added to the flow tube. The lines indicate the expected OH concentration from published OH yields. The black triangles in the top plot reflect the predicted concentration of stabilized Criegee intermediates by the Master Chemical Mechanism (MCM SCI) (see text).

Measurements of the OH radical yield from the ozonolysis of biogenic alkenes: A potential interference with laser-induced fluorescence measurements of ambient OH

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Supplementary Information

Table S1: Calibration factors for the different inlet lengths and pressures used in these experiments

Nozzle diameter (mm)	Inlet length (mm)	Pressure (Torr)	Calibration factor (counts cm^3 mW^{-1})	LOD (S/N=1, 10 min) (cm^{-3})
0.6	32	4	2.11E-07	5.03E+05
0.6	32	7	1.41E-07	8.38E+05
0.6	32	9	1.07E-07	1.28E+06
0.6	140	4	1.36E-07	8.55E+05
0.6	140	7	1.01E-07	1.23E+06
0.6	140	9	5.65E-08	2.14E+06
0.6	248	4	8.03E-08	1.33E+06
0.6	248	7	5.13E-08	2.19E+06
0.6	248	9	3.85E-08	3.76E+06
1.0	32	5	1.93E-07	5.63E+05
1.0	32	7	1.46E-07	7.78E+05
1.0	32	9	1.19E-07	9.63E+05
1.0	140	5	1.39E-07	8.79E+05
1.0	140	7	1.25E-07	1.24E+06
1.0	140	9	7.77E-08	1.71E+06
1.0	248	5	1.08E-07	1.03E+06
1.0	248	7	8.01E-08	1.54E+06
1.0	248	9	5.64E-08	1.95E+06

Table S2: Summary of several individual ozonolysis experiments

BVOC	Concentration	Inlet (mm)	Nozzle (mm)	Pressure (Torr)	OH w/ Interference	OH W/O Interference	$[O_3]$ (cm^{-3})	Interference (cm-3)	Interference (%)
α-pinene	3.00E+12	32	0.6	4	8.05E+07	3.82E+07	4.12E+13	4.06E+07	50.44
		32	0.6	4	1.09E+08	3.86E+07	6.63E+13	6.98E+07	64.20
		32	0.6	4	1.91E+08	9.88E+07	9.04E+13	9.20E+07	48.23
		32	0.6	7	1.67E+08	8.22E+07	6.80E+13	8.67E+07	51.99
		32	0.6	7	8.19E+07	3.67E+07	4.03E+13	4.54E+07	55.40
		32	0.6	7	2.02E+08	9.29E+07	8.51E+13	1.10E+08	54.34
		32	0.6	9	1.01E+08	4.65E+07	4.30E+13	5.27E+07	52.05
		32	0.6	9	1.45E+08	6.45E+07	6.72E+13	8.13E+07	55.94
		32	0.6	9	2.04E+08	7.91E+07	8.95E+13	1.26E+08	61.72
		32	1.0	5	6.93E+07	3.61E+07	3.67E+13	3.42E+07	49.38
		32	1.0	5	1.37E+08	7.88E+07	7.25E+13	5.72E+07	41.71
		32	1.0	5	2.00E+08	1.22E+08	9.31E+13	7.70E+07	38.49
		32	1.0	7	8.94E+07	4.27E+07	3.76E+13	4.69E+07	52.52
		32	1.0	7	1.48E+08	8.33E+07	7.25E+13	6.54E+07	44.19
		32	1.0	7	2.04E+08	1.19E+08	9.85E+13	9.19E+07	44.99
		32	1.0	9	1.44E+08	8.11E+07	6.27E+13	6.16E+07	42.75
		32	1.0	9	1.29E+08	7.66E+07	4.83E+13	5.29E+07	41.02
		32	1.0	9	2.07E+08	9.71E+07	9.00E+13	1.08E+08	52.15
		140	0.6	4	1.36E+08	4.70E+07	3.94E+13	6.27E+07	46.14
		140	0.6	4	1.94E+08	1.00E+08	6.55E+13	6.25E+07	32.22
		140	0.6	4	2.84E+08	1.37E+08	9.22E+13	8.16E+07	28.74
		140	0.6	7	1.09E+08	6.44E+07	3.69E+13	4.50E+07	41.18
		140	0.6	7	1.89E+08	8.02E+07	6.72E+13	1.09E+08	57.57
		140	0.6	7	2.62E+08	1.44E+08	9.07E+13	1.17E+08	44.71
		140	0.6	9	1.60E+08	5.66E+07	3.31E+13	1.05E+08	65.58
		140	0.6	9	2.29E+08	1.52E+08	6.85E+13	7.78E+07	33.93
		140	0.6	9	3.93E+08	1.70E+08	9.04E+13	2.21E+08	56.35
		140	1.0	5	1.47E+08	7.38E+07	2.95E+13	7.34E+07	49.79
		140	1.0	5	2.33E+08	1.40E+08	7.25E+13	9.37E+07	40.20
		140	1.0	5	2.82E+08	1.39E+08	9.04E+13	1.33E+08	47.16
		140	1.0	7	1.27E+08	7.62E+07	3.22E+13	4.85E+07	38.26
		140	1.0	7	2.32E+08	1.53E+08	7.39E+13	7.77E+07	33.44
		140	1.0	7	3.44E+08	2.39E+08	9.54E+13	1.01E+08	29.25
		140	1.0	9	1.92E+08	1.32E+08	3.22E+13	5.77E+07	30.05
		140	1.0	9	3.23E+08	2.27E+08	7.39E+13	9.44E+07	29.22
		140	1.0	9	4.10E+08	2.97E+08	9.40E+13	1.09E+08	26.63
		248	0.6	4	9.82E+07	1.30E+07	4.30E+13	8.56E+07	87.14
		248	0.6	4	2.45E+08	5.39E+07	6.98E+13	1.94E+08	78.91
		248	0.6	4	3.39E+08	8.35E+07	8.46E+13	2.58E+08	76.12
		248	0.6	7	1.78E+08	7.27E+07	3.09E+13	1.03E+08	58.06
		248	0.6	7	2.14E+08	6.50E+07	7.25E+13	1.45E+08	67.92
		248	0.6	7	4.57E+08	1.71E+08	9.00E+13	2.94E+08	64.22
		248	0.6	9	2.01E+08	1.16E+08	3.49E+13	8.64E+07	43.02

BVOC	Concentration	Inlet (mm)	Nozzle (mm)	Pressure (Torr)	OH w/ Interference	OH W/O Interference	$[O_3]$ (cm^{-3})	Interference (cm-3)	Interference (%)
α-pinene	3.00E+12	248	0.6	9	3.66E+08	1.49E+08	7.12E+13	2.09E+08	57.06
		248	0.6	9	5.56E+08	3.06E+08	8.86E+13	2.39E+08	42.90
		248	1.0	5	1.42E+08	5.02E+07	3.22E+13	8.90E+07	62.78
		248	1.0	5	2.30E+08	7.93E+07	6.72E+13	1.51E+08	65.82
		248	1.0	5	3.48E+08	8.66E+07	9.13E+13	2.57E+08	73.88
		248	1.0	7	4.34E+08	1.07E+08	3.31E+13	3.26E+08	75.06
		248	1.0	7	8.32E+08	1.72E+08	6.72E+13	6.55E+08	78.69
		248	1.0	7	1.08E+09	2.77E+08	9.49E+13	8.01E+08	73.97
		248	1.0	9	4.94E+08	1.13E+08	2.95E+13	3.84E+08	77.72
		248	1.0	9	9.59E+08	4.03E+08	6.72E+13	5.90E+08	61.53
		248	1.0	9	1.41E+09	3.17E+08	9.49E+13	1.08E+09	76.23
Ocimene	1.00E+13	32	0.6	4	1.03E+08	1.80E+07	4.03E+13	8.48E+07	82.04
		32	0.6	4	1.67E+08	3.87E+07	6.54E+13	1.28E+08	76.45
		32	0.6	4	1.97E+08	5.09E+07	8.51E+13	1.48E+08	75.16
		32	1.0	5	1.48E+08	3.89E+07	4.43E+13	1.10E+08	74.01
		32	1.0	5	1.72E+08	4.45E+07	6.18E+13	1.28E+08	74.30
		32	1.0	5	2.51E+08	5.58E+07	9.80E+13	1.94E+08	77.28
		140	0.6	4	1.08E+08	1.35E+07	4.30E+13	9.29E+07	85.78
		140	0.6	4	1.37E+08	1.29E+07	5.91E+13	1.23E+08	90.04
		140	0.6	4	1.91E+08	1.78E+07	8.51E+13	1.74E+08	91.07
		140	1.0	5	1.09E+08	1.28E+07	4.21E+13	9.72E+07	89.35
		140	1.0	5	1.52E+08	1.54E+07	6.58E+13	1.38E+08	90.69
		140	1.0	5	1.98E+08	2.72E+07	8.60E+13	1.76E+08	88.86
		248	0.6	4	1.33E+08	2.21E+07	4.03E+13	1.11E+08	82.99
		248	0.6	4	1.83E+08	2.07E+07	6.00E+13	1.49E+08	81.42
		248	0.6	4	2.46E+08	4.30E+07	8.86E+13	2.27E+08	92.43
		248	1.0	5	1.06E+08	1.22E+07	4.03E+13	9.36E+07	88.25
		248	1.0	5	1.48E+08	4.77E+07	6.85E+13	9.95E+07	67.32
		248	1.0	5	1.79E+08	2.42E+07	8.68E+13	1.55E+08	86.33
β-Pinene	1.83E+13	32	0.6	4	7.30E+06	4.08E+06	2.95E+13	4.19E+06	57.36
		32	0.6	4	1.23E+07	8.49E+06	5.55E+13	4.23E+06	34.25
		32	0.6	4	1.93E+07	1.34E+07	8.06E+13	5.97E+06	30.93
	1.12E+11	32	0.6	4	1.41E+07	1.09E+07	8.15E+13	4.53E+06	32.25
		32	0.6	4	9.47E+06	4.17E+06	5.55E+13	5.46E+06	57.65
		32	0.6	4	6.28E+06	2.64E+06	3.04E+13	3.57E+06	56.88
		32	0.6	4	2.12E+07	1.50E+07	8.24E+13	5.05E+06	23.75
		32	0.6	4	1.57E+07	1.11E+07	5.73E+13	5.11E+06	32.46
		32	0.6	4	9.91E+06	7.22E+06	2.69E+13	2.75E+06	27.78

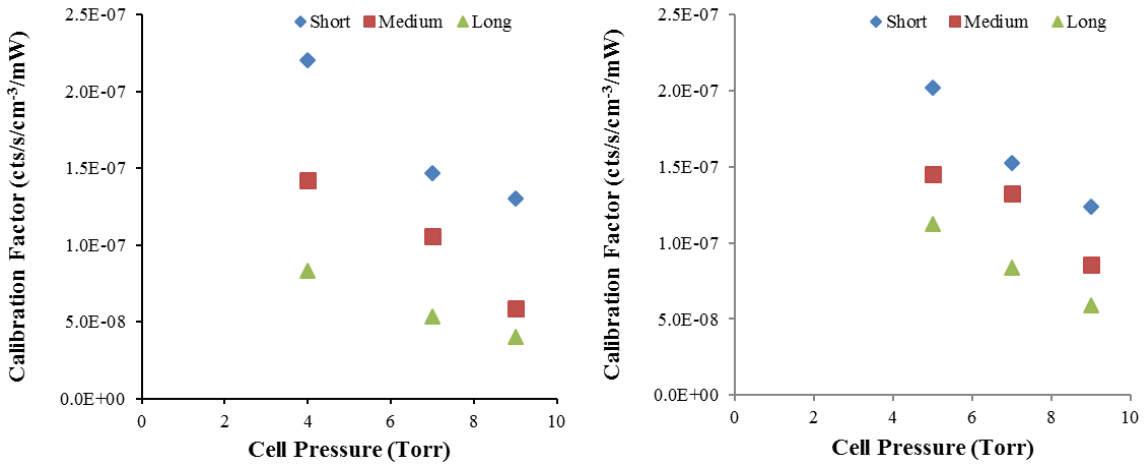

Figure S1. Calibration factors based on inlet length and diameter for the 1 mm diameter inlet (left) and the 0.6 mm diameter inlet (right).

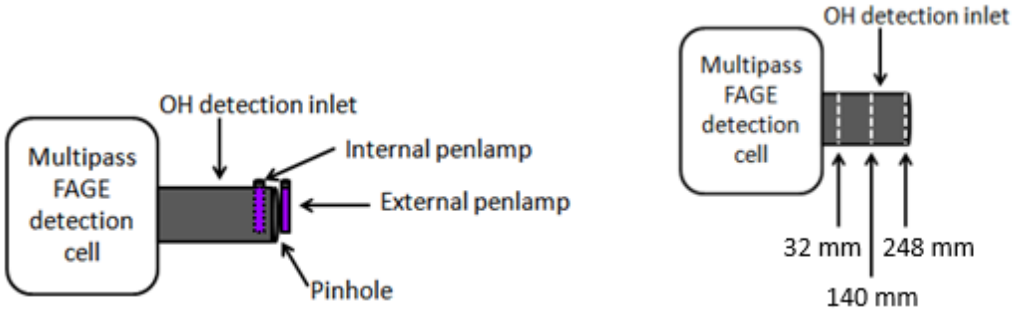

Figure S2. Placement of mercury penlamps to determine the efficiency of the external OH titration (left) and the varying inlet lengths used in the experiments (right).

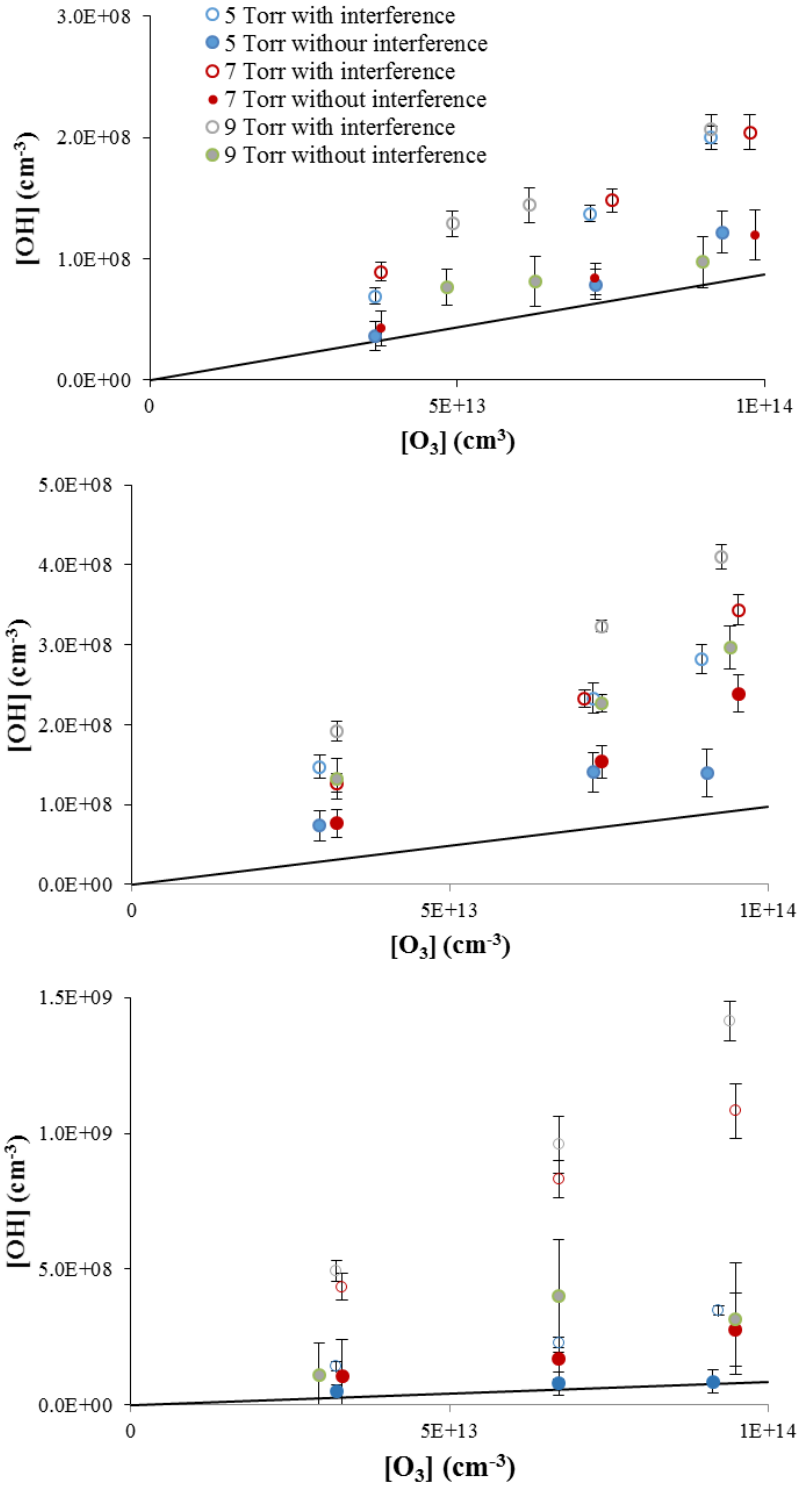

Figure S3. OH concentrations from α-pinene ozonolysis at 3 cell pressures with and without the interference using the 1 mm inlet and the short (top), medium (middle), and long (bottom) inlet lengths. Error bars indicate the precision of the measurement (1σ). Lines indicate the expected steady-state OH concentration based on published values of the OH yield.

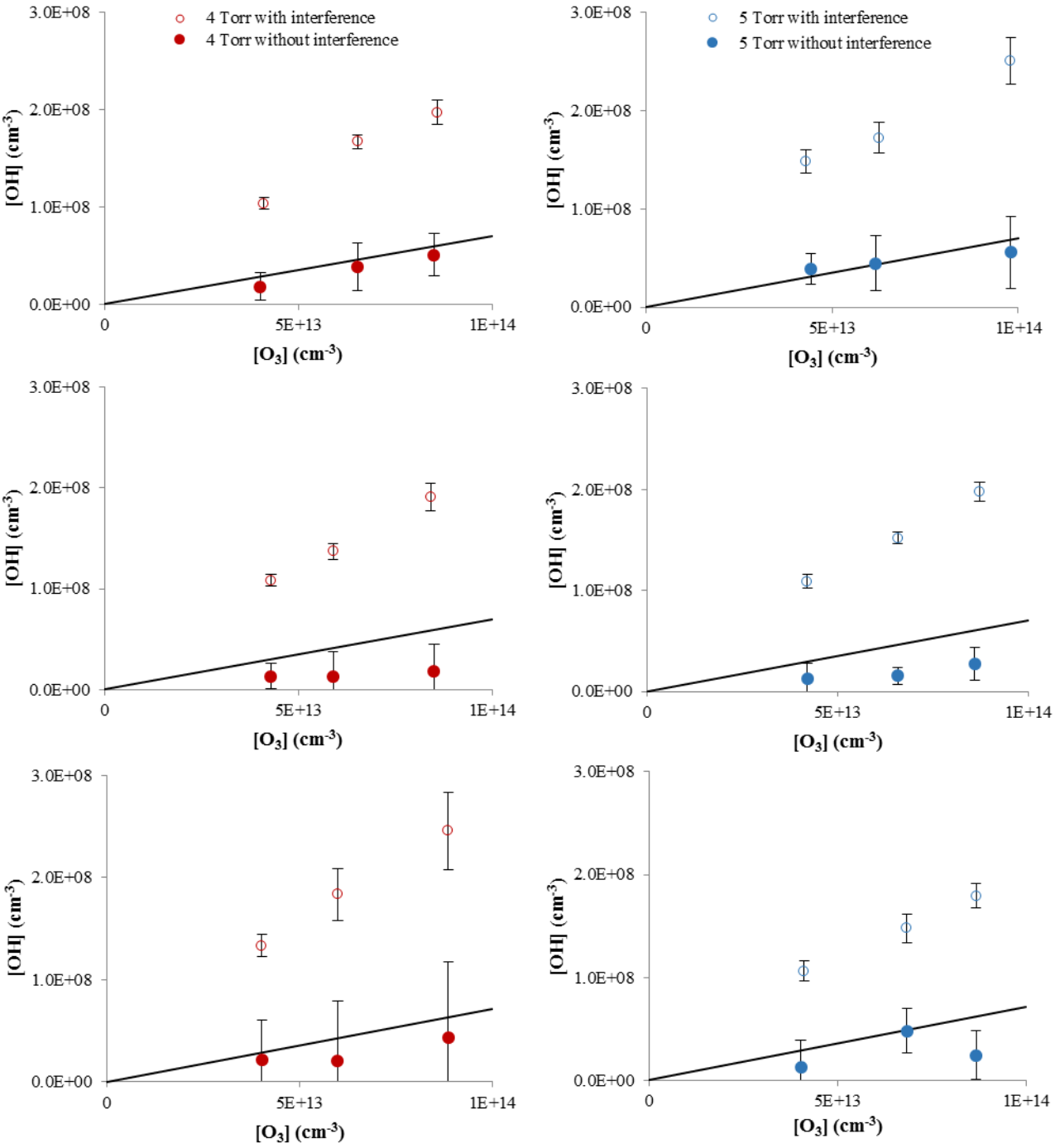

Figure S4. OH concentrations from ocimene ozonolysis with an ocimene concentration of 1×10^{13} molecules cm^{-3}. The left column shows the results using the 0.6 mm inlet diameter and the right column using the 1 mm inlet diameter. The top row shows results from the short inlet length, middle row from the medium inlet, and the last row from the long inlet length. Error bars indicate the precision of the measurement (1σ). Lines indicate the expected steady-state OH concentration based on published values of the OH yield.

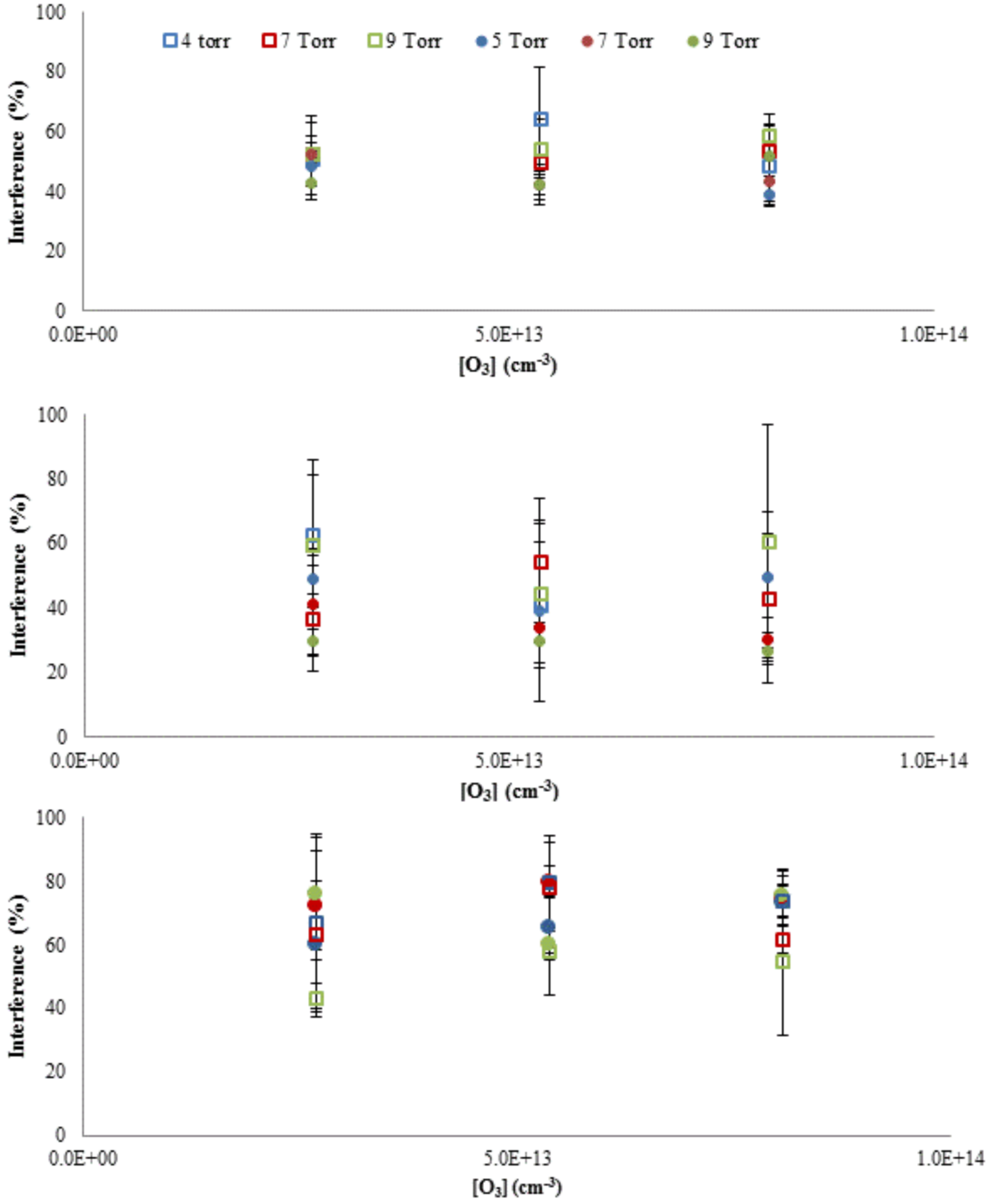

Figure S5. Interference percentages from α-pinene ozonolysis at 3 cell pressures (in Torr) (Table S1). Filled circles show measurements using the 1 mm inlet and the open squares measurement using the 0.6 mm inlet using the short (top), medium (middle), and long (bottom) inlet lengths. Error bars indicate the precision of the measurement (2σ).

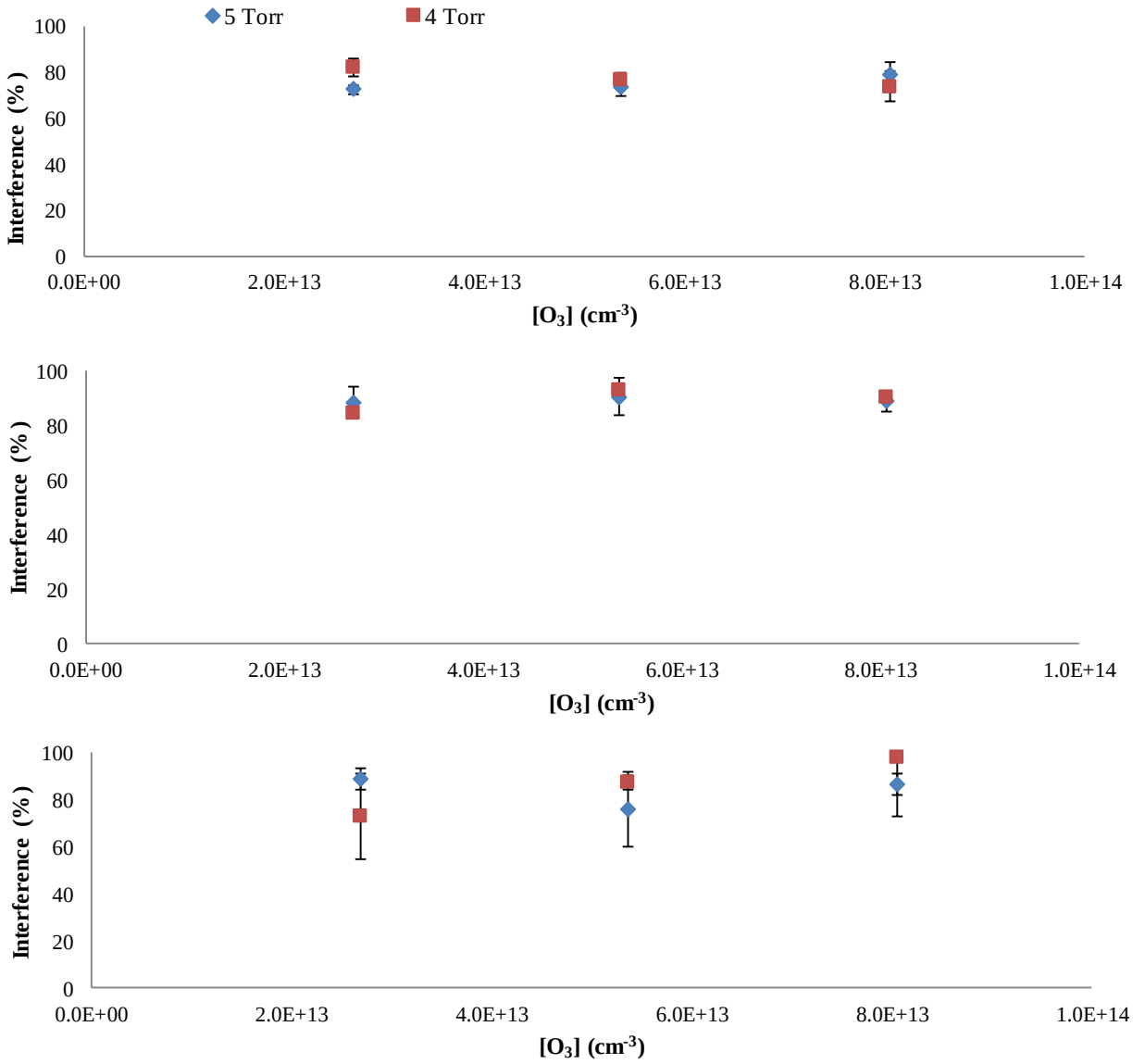

Figure S6. Interference percentages from the ozonolysis of ocimene with an ocimene concentration of approximately 1×10^{13} cm^{-3}. The blue circles represent results using the 1 mm inlet diameter at 5 Torr and the red circles represent results using the 0.6 mm inlet diameter at 4 Torr. Top plot shows the results for the short inlet, middle plot shows results for the medium inlet, and the bottom plot shows results for the long inlet. Error bars represent the precision of the measurements (2σ).