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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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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 several BVOCs 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 and BVOC concentrations was observed that was not laser generated and was independent of the ozonolysis reaction time. 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.

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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). 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 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 their 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 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 (Schlossler et al., 2007). A subsequent intercomparison inside the SAPHIR chamber found that measurements from several different LIF-FAGE instruments under a

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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 (up to 28 ppm) and trans-2-butene (greater than 12 ppb). 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).

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.

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. 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

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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. 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). 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 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. 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 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}) and measured using a Teledyne Photometric Ozone Analyzer (model 400E).

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

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experiment, with approximate concentrations of 2×10^{11} to 4×10^{13} molecules cm^{-3} for α-pinene, 1×10^{11} to 4×10^{13} molecules cm^{-3} for β-pinene, and 9×10^{10} to 5×10^{13} molecules cm^{-3} for ocimene.

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.

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

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approximately 20 seconds. These measurements are recorded for at least 5 cycles per ozone concentration once the OH concentration has stabilized.

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. 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 (4.5 cm, 14 cm, and 23.5 cm) (Fig. S1). 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 4×10^5 - 3×10^6 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, 1% in N_2, Matheson) was added through a circular injector surrounding the detection inlet to chemically remove external OH (Griffith et al., 2016) (Fig. 2). 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). 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 IU LIF-FAGE 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 flow of approximately 3-5 sccm). 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.

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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. Any OH that was measured using spectral modulation after C_3F_6 addition would, therefore, 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.

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 (approximately 20 ms), 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 (W/int), and the filled symbols represent the OH signal after the signal measured with C_3F_6 addition is removed (W/O int) using the 0.6 mm nozzle. 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:

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

In this equation, k_{O3} is the rate constant for the O_3 + alkene reaction with an OH yield of α, k_{OH} 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 before (Hansen et al., 2014). 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 as well as wall loss of OH 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.

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. 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

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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 producing an OH yield of approximately 0.81 ± 0.10, determined from 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). Similar results were observed with the use of the 1 mm nozzle diameter (Fig. S3). These results are comparable 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 changing cell pressures in these experiments were obtained by changing the pumping speed, which likely impacts the velocity and residence time of the airstream inside the detection cell. This suggests that increasing the reaction time for the shortest 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. These results appear to be independent of the α-pinene concentration (Fig. 4, top) as the level of the interference is similar for 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. Similar to that observed for the ozonolysis of α-pinene, the interference and the observed OH yield did not significantly 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- and β-pinene, the interference and

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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 ± 0.9 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 likely 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 higher reactivity of α-pinene, β-pinene, and ocimene with ozone compared to that of isoprene and MBO under the conditions of these experiments, and 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.

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):

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

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

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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 (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 as a function of the turnover rate appears to be similar to that observed by Fuchs et al. (2016). However, this agreement may be fortuitous, as differences in the design of the individual instruments may impact the level of the interference.

The interference signals from the ozonolysis of 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. Similar results were observed for the ozonolysis of ocimene (Fig. S6), with average percent interferences of 75 ± 1%, 89 ± 2%, and 83 ± 2%, for the short, medium, and long inlets respectively with the 1

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mm nozzle, and 78 ± 1%, 89 ± 1%, and 86 ± 2%, for the short, medium, and long inlets, respectively with the 0.6 mm nozzle (Fig. S6).

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 on the ozonolysis reaction time, suggesting that the interference is not due to a stable oxidation product but may be due to a steady-state intermediate in the ozonolysis mechanism, as an interference due to stable oxidation products would likely increase with reaction time. 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.

3.3 Stabilized Criegee intermediates 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 long reaction times. At short 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).

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 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.

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However, 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). 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}. 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. 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 OH signal including the 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 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).

The magnitude of the interference observed in these experiments was consistent with the expected steady-state concentration of stabilized Criegee intermediates in the flow tube determined 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). 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, 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. 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.

However, 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 Creigee 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). These results also appear to be consistent with the observations by Hard et al.

(2002), who found that an interference associated with their alkene ozonolysis calibration experiments disappeared in the presence of 1% water vapor. Given the potentially rapid reaction of Criegee intermediates with water vapor (Chao et al., 2015), this suggests that the source of their interference was also the decomposition of Criegee intermediates inside their detection cell. 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. However, Dusanter et al. (2008) found that the instrument sensitivities derived from the ozone-alkene calibration technique 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.

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,

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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).

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 mixing ratios of isoprene were less than 2 ppb and daytime maximum ozone mixing ratios were approximately 30 ppb on average. During CalNex, mixing ratios of isoprene were even lower, less than 1 ppb on average, although 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) (Griffith et al., 2016).

In contrast, recent measurements of OH concentrations by the IU-FAGE instrument in an Indiana forest using the external chemical titration technique under relatively warmer conditions, with isoprene mixing ratios greater than 4 ppb and higher daytime maximum ozone mixing ratios (approximately 40 ppb) did reveal an interference that correlated with both temperature and ozone concentrations, similar to the results of Mao et al. (2012) (Lew et al., 2017). 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). However, similar to that observed by Novelli et al. (2016), estimates of the ambient concentration of SCIs on the order of approximately $4\text{-}5\times10^4$ 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 (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 eliminated the interference, 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 potential interference, future measurements of OH by the IU-FAGE instrument will involve a detection cell design that minimizes both reaction time and potential surface collisions.

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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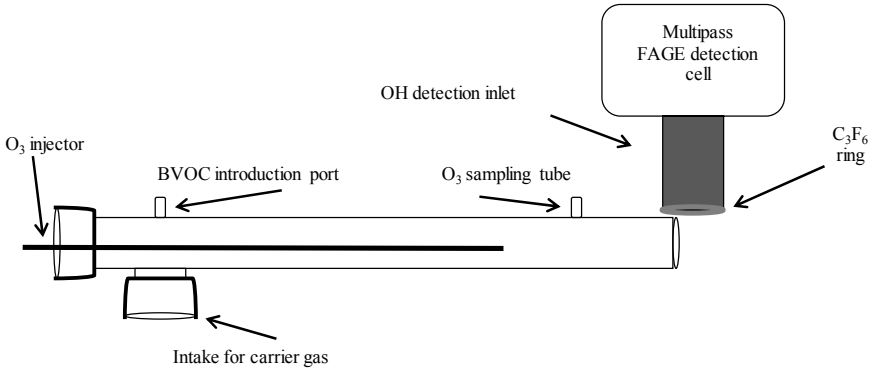

Figure 1: Schematic of the atmospheric pressure flow system used in this study.

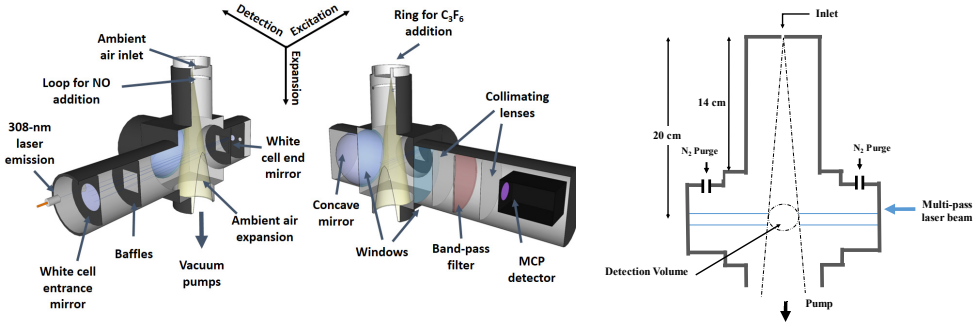

Figure 2. Schematic of the IU-FAGE sampling/excitation axis (left) and cross section with dimensions for the medium inlet configuration (right).

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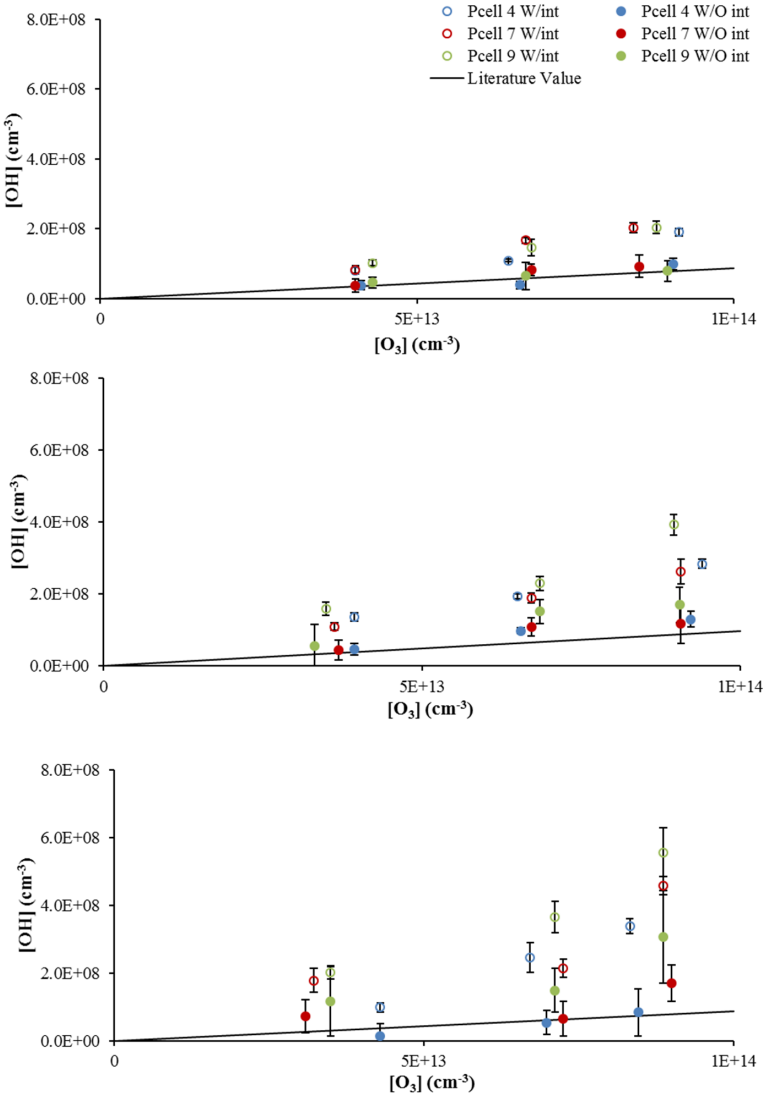

Figure 3. OH concentrations from α-pinene ozonolysis at three cell pressures with and without the interference using the 0.6 mm diameter nozzle and the short (top), medium (middle), and long (bottom) inlet lengths with α-pinene concentrations of approximately 3×10^{12} cm^{-3}. Error bars indicate the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

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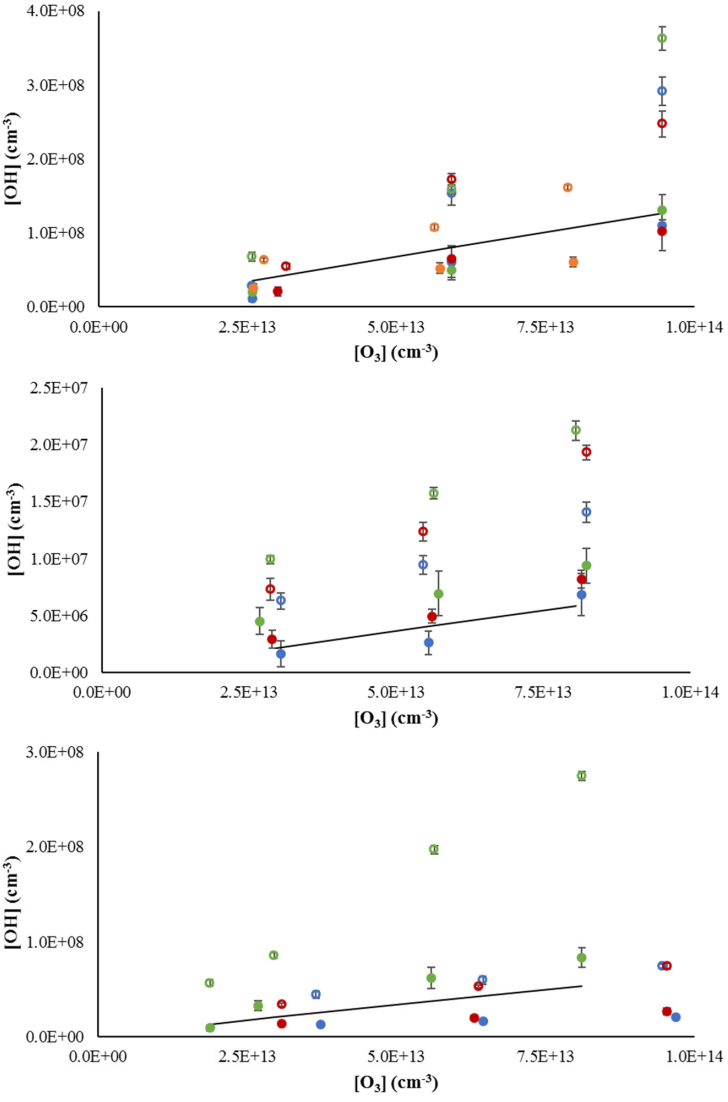

Figure 4. OH concentrations using the short inlet from the ozonolysis of α-pinene (top, 1×10^{12}-4×10^{13} cm^{-3}), β-pinene (middle, 1×10^{11}-4×10^{13} cm^{-3}), and ocimene (bottom, 2×10^{11}-5×10^{13} cm^{-3}). Open circles indicate measurements with the interference, filled circles without the interference. Colors indicate relative concentrations (orange>green>red>blue). Solid lines reflect the expected OH radical yield (see text). Error bars reflect the measurement precision (1σ).

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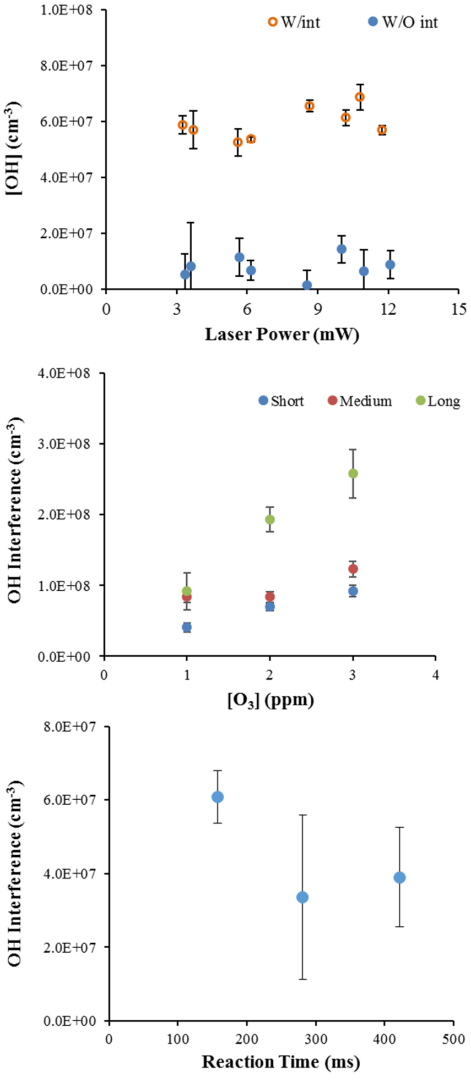

Figure 5. OH concentrations from ocimene ozonolysis with varied laser power at an ozone mixing ratio of 2 ppm and ocimene concentration of approximately 3×10^{13} cm^{-3} (top). OH interference during α-pinene ozonolysis based on ozone concentration and inlet length with an α-pinene concentration of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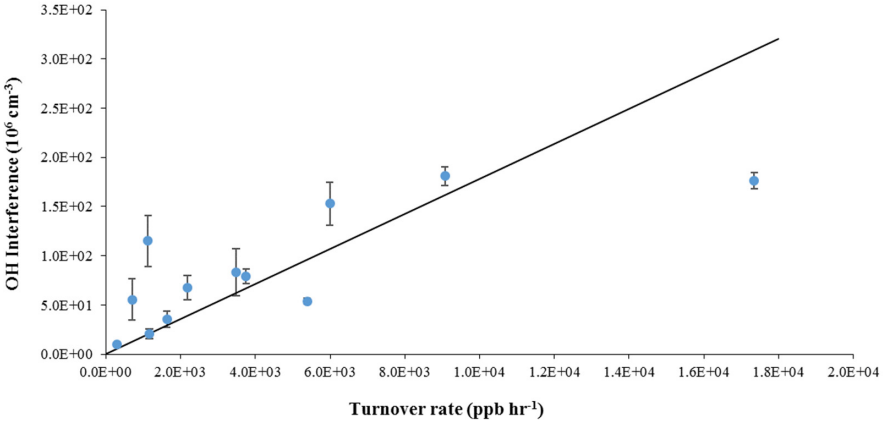

Figure 6. Interference signal as a function of turnover rate for the ozonolysis of α-pinene using the short inlet. Solid line reflects the slope observed by Fuchs et al. (2016).

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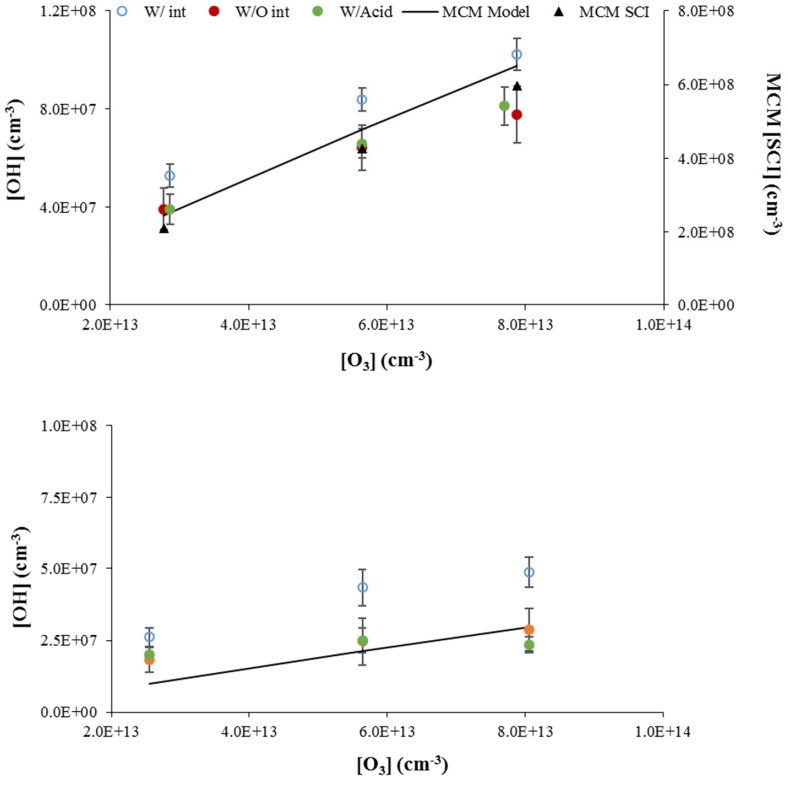

Figure 7. Measurements of OH concentrations from the ozonolysis of α-pinene (approximately 1×10^{12} cm^{-3}, top) and ocimene (approximately 4×10^{11} cm^{-3}, bottom). Open symbols are measurements including the interference, filled red circles are the resulting OH measurements when the interference 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 (see text).