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Identification and quantification of carbonyl-containing α-pinene ozonolysis products using *O-tert*-butylhydroxylamine hydrochloride

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Abstract The yields of carbonyl-containing reaction products from the ozonolysis of α-pinene have been investigated using concentrations of ozone found in the indoor environment ($[O_3] \leq 100$ ppb). An impinger was used to collect gas-phase oxidation products in water, where the derivatization agent *O*-tert-butylhydroxylamine hydrochloride (TBOX) and gas chromatography-mass spectrometry were used to identify carbonyl-containing species. Seven carbonyl-containing products were observed. The yield of the primary product, pinonaldehyde was measured to be 76 %. Using cyclohexane as a hydroxyl radical (·OH) scavenger, the yield of pinonaldehyde decreased to 46 %, indicating the influence secondary OH radicals have on α-pinene ozonolysis products. Furthermore, the use of TBOX, a small molecular weight derivatization agent, allowed for the acquisition of the first mass spectral data of oxopinonaldehyde, a tricarbonyl reaction product of α-pinene ozonolysis. The techniques described herein allow for an effective method for the collection and identification of terpene oxidation products in the indoor environment.

Keywords Ozonolysis · Reaction products · Derivatization · α-Pinene · Sampling · Terpene

1 Introduction

Since most people spend between 70 and 90 % of their time indoors, it is acknowledged that indoor air pollutants can make a substantial contribution to time-weighted exposures to many

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compounds (Samet et al. 1987, 1988). In particular, building occupants, especially cleaning personnel, are exposed to a wide variety of airborne chemicals when cleaning agents and air fresheners are used in buildings (Nazaroff and Weschler 2004). Several epidemiological studies have identified associations between exposure to cleaning and respiratory effects, although the causative chemical or class of chemicals remain to be identified (Henneberger et al. 2003; Mendonça et al. 2003; Rosenman et al. 2003). One class of compounds commonly used in these solutions, terpenes, are highly reactive with important indoor oxidants such as ozone (O_3) and hydroxyl radicals (·OH) due to the presence of carbon-carbon double bonds in their structure. These reactions form highly oxidized species, including ketone and aldehyde products, which have been implicated in a number of deleterious health effects including occupational asthma (Jarvis et al. 2005).

(+)-α-Pinene ((1*R*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene) is one such terpene found in a variety of cleaning products used in occupational settings (Colombo et al. 1991; Zhu et al. 2001). α-Pinene is a ten-carbon bicyclic hydrocarbon with an endocyclic double bond and, therefore, reacts quickly with O_3 and ·OH (5.7×10^{-16} and 1.2×10^{-11} cm^3 $molecules^{-1}$ s^{-1}, respectively) (Eddingsaas et al. 2012; Gill and Hites 2002; Khamaganov and Hites 2001). The identification and quantification of α-pinene oxidation products in reaction chamber experiments have been monitored by real-time measurements, using Fourier transform infrared spectroscopy (Brusse et al. 2008; Orlando et al. 2000) or atmospheric pressure chemical ionization-mass spectrometry (Warscheid and Hoffmann 2001; Müller et al. 2008). These on-line techniques are beneficial, since they allow for a direct insight into the product formation process; however, the specialized instrumentation may not be suitable when field sampling is needed. In these cases, methods involving cryotraps (Yokouchi and Ambe 1985), cartridges (Hakola et al. 1994; Grosjean et al. 1992; Kotzias et al. 1991), denuders (Yu et al. 1999), filters (Yasmeen et al. 2010; Surratt et al. 2007; Surratt et al. 2008; Kahnt et al. 2014; Szmigielski et al. 2007), or high-volume dichotomous samplers (Claeys et al. 2009; Claeys et al. 2007), followed by thermal desorption or solvent extraction have been utilized. These samples are then injected onto GC or LC columns, typically after a derivatization step when analyzing aldehydes, ketones, or carboxylic acids (Wells and Ham 2014; Lu et al. 2013).

While both the O_3 and ·OH oxidation of α-pinene have been extensively studied using a variety of techniques, large uncertainties in the identity and yields of its reaction products remain (Eddingsaas et al. 2012). For example, the reported yield of pinonaldehyde from the oxidation of α-pinene by ·OH ranges from 3 to 87 % (Nozière et al. 1999; Eddingsaas et al. 2012). Moreover, a survey of the literature shows that the majority of studies investigating α-pinene ozonolysis have used ozone concentrations ranging from 100 ppb to 20 ppm, concentrations that are well above oxidant concentrations found in indoor environments (Glasius et al. 2000; Winterhalter et al. 2003; Koch et al. 2000; Ma et al. 2008).

In this study, we describe a method for quantification of products resulting from terpene ozonolysis in which we utilize a Teflon impinger to capture gas-phase reaction products in water. Yields of products from the oxidation of α-pinene under conditions found in indoor environments were determined, focusing on carbonyl-containing products due to their potential health effects (Anderson et al. 2012). Experiments were performed both in the presence and absence of cyclohexane to determine the influence secondary ·OH have on the overall yield of ozonolysis products. Additionally, by utilizing a low molecular weight derivatization agent, we are able to provide, for the first time, the mass spectral information for oxopinonaldehyde, a tricarbonyl reaction product of α-pinene ozonolysis. A formation mechanism is proposed based on the observation that the yield of oxopinonaldehyde increases when peroxyl radical concentrations increase.

2 Materials and methods

2.1 Chemicals and solvents

All compounds were used as received and had the following purities: from Sigma-Aldrich/Fluka (St. Louis, MO): *O-tert*-Butylhydroxylamine hydrochloride (TBOX, 99 %), (+)-α-pinene (≥99 %), toluene (HPLC grade, ≥99 %), cyclohexane (HPLC grade, ≥99 %), 2-butanol (anhydrous, 99.5 %), glyoxal (40 wt.% in water), methylglyoxal (40 wt.% in water), and glutaraldehyde (50 wt.% in water). Methanol (HPLC grade ≥ 99 %) and cyclohexanone (99.8 %) were from Fisher Scientific. Deionized water (DI H_2O) was distilled, deionized to a resistivity of 18 MΩ cm, and filtered using a Milli-Q® filter system (Billerica, MA). Helium (UHP grade), the carrier gas, was supplied by Butler Gas (McKees Rocks, PA) and used as received.

Experiments were carried out at 297 ± 3 K and 1 atm in an 80 L reaction chamber constructed from 5-mil FEP Teflon film (Welch Fluorocarbon Inc., Dover, NH). Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This treated dry air from the NIOSH facility flowed through a mass flow controller and into a humidifying chamber and was subsequently mixed with dry air to the pre-determined relative humidity (RH) of 50 %. The 80 L Teflon reaction chamber was equipped with a heated syringe injection port constructed of a 6.4-mm Swagelok (Solon, OH) tee fitting with a 10 mm Ice Blue septum (Restek, Bellefonte, PA) which allowed for the introduction of liquid reactants into the chamber. All reactant mixtures were generated by this system. Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon chamber. Aliquots of this O_3/air mixture were added to the 80 L Teflon reaction chamber using a gas-tight syringe. Background measurements of the NIOSH facility air showed concentrations of O_3, NO, and NO_2 at less than 1.0, 1.2, and 0.5 ppb, respectively. O_3 concentrations were measured using a Thermo Electron (Waltham, MA) ultraviolet photometric ozone analyzer Model 49C. Background NO and NO_2 concentrations were measured using a Thermo Electron (Waltham, MA) NOx analyzer Model 49i.

2.2 System calibration

Cyclohexanone, glyoxal, methylglyoxal, and glutaraldehyde were used to calibrate for products from the α-pinene/O_3 reaction system using a modified version of a previously reported technique (Wells and Ham 2014). Briefly, calibration plots were made by analyzing triplicate measurements of standard solutions that were injected into the 80 L Teflon reaction chamber at 50 % RH, ranging in concentration from 5 to 30 ppb ($1.2–7.4 \times 10^{11}$ molecule cm^{-3}). Samples were obtained by pulling 60 L of air using a pump (URG 3000-02Q, Chapel Hill, NC) from the chamber into 25 mL of deionized water in a 60 mL Teflon impinger (Savillex, Eden Prairie, MN). After collection, samples were transferred to 40 mL glass vials, then derivatized with 100 μL aqueous 250 mM TBOX, and placed in a heated water bath at 70 °C for 2 h. After removing the vial from the water bath and allowing to cool to room temperature, 0.5 mL of toluene was added to the vial. The vial was shaken for 30 s and the organic phase and aqueous phase were allowed to separate. A 100 μL aliquot was taken from the organic phase and placed in a 2 mL autosampler vial with a 100 μL glass insert (Restek, Bellefonte, PA).

2.3 α-Pinene + O_3 reactions

In an 80 L volume of air at 50 % RH, O_3 (20–100 ppb; 0.5–2.5 x 10^{12} molecule cm^{-3}) was added to 1.7 ppm (+)-α-pinene (4.25 x 10^{13} molecule cm^{-3}), and allowed to react for 30 min. After the reaction, 60 L of sample was collected, at 4 L/min, through 25 mL of deionized water using an impinger (as described above). The samples were then TBOX derivatized and extracted as described above. Additional experiments included the addition of 283 ppm (7.0 x 10^{15} molecule cm^{-3}) cyclohexane or 334 ppm 2-butanol (8.2 x 10^{15} molecule cm^{-3}) to scavenge OH radicals formed from Criegee intermediates of α-pinene ozonolysis to gain information on secondary product formation chemistry (Docherty and Ziemann 2003). Control experiments conducted with a 400 mm denuder (URG-2000-30B5, URG, Chapel Hill, NC) coated with ground XAD-4 resin (average particle size 0.7 μm) in line before the impinger led to no products being seen in the impinger sample suggesting that all observed products are in the gas-phase. The results from each of these experiments are described below. Each experiment was done in triplicate.

2.4 GC-MS analysis

All samples were analyzed using an Agilent (Santa Clara, CA) 7890B GC coupled to an Agilent 240 Internal EI/CI ion trap mass spectrometer. Samples were analyzed in both electron ionization (EI) and chemical ionization (CI) modes with liquid methanol serving as the CI reagent. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 μm film thickness) column and the following GC oven parameters: 40 °C for 2 min, then 5 °C min^{-1} to 200 °C, then 25 °C min^{-1} to 280 °C and held for 5 min. One μL of each sample was injected in the splitless mode with the injector temperature at 130 °C. The ion trap mass analyzer was tuned using perfluorotributylamine (FC-43). Full-scan mass spectra were collected in the *m/z* range 40–1000.

3 Results and discussion

3.1 System calibration

Quantitative determination of reaction products identified in the α-pinene/O_3 experiments was made possible by using calibration factors, recoveries, and collection efficiencies of known concentrations of standard compounds. Standard solutions were purchased from Sigma Aldrich and used to quantify the observed reaction products cyclohexanone, glyoxal, and methylglyoxal. Standards for the remaining detected products were not commercially available, so quantification was estimated by using a surrogate dicarbonyl compound, glutaraldehyde. Previous studies have estimated that when using a structurally similar surrogate the associated error for yields is roughly ±30 % (Glasius et al. 2000; Jaoui and Kamens 2001; Yu et al. 1999). The retention times for the derivatized standard compounds were 13.8 min for cyclohexanone, 15.3 min for glyoxal, 16.2 min for methylglyoxal, and 22.0, 22.2, and 22.5 min for glutaraldehyde. The occurrence of multiple peaks for a single compound is a common phenomenon for oximes, like TBOX-derivatized glutaraldehyde, as they have stereoisomers that can be resolved by a GC column (Kourtchev et al. 2012; Yu et al. 1995; Yu et al. 1998). When integrating peak areas, all stereoisomer peaks for a compound were used. Calibration plots are shown in Fig. S1.

3.2 α-Pinene + O_3 experiments

Seven carbonyl-containing products from α-pinene ozonolysis were observed and are described in Table 1. Identification of products is made possible by analyzing both the CI and EI spectra. In the EI spectra, due to the *tert*-butyl ($C_4H_9^+$) fragments from the oximes the relative abundance of the *m/z* 57 ion was greater than 25 % and could be effectively used to generate selected ion chromatograms to identify derivatized carbonyl compounds. The ease of the loss of the tert-butyl fragment often makes the molecular ion challenging to distinguish in an EI spectrum; however, an $[M + H]^+$ ion was readily observed for the derivatized oxime compounds when analyzed by CI (Figs. 1 & 2).

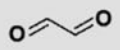
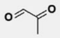
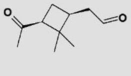
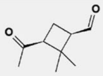
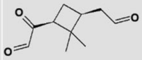
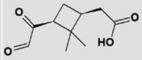
The chromatographic peaks for the oxime observed at 24.8, 25.3, 28.8, 29.2, 29.6, and 30.0 min are derivatized versions of pinonaldehyde, the major product of α-pinene ozonolysis. Tentative peak assignments to a specific stereoisomer based on chromatographic and mass spectral data can be seen in Fig. S2. The two earliest eluting peaks correspond to singly-derivatized pinonaldehyde while the four later peaks result from doubly-derivatized pinonaldehyde. In a previous study using TBOX, none of the multi-carbonyl compounds detected resulted in partial derivatization (Wells and Ham 2014). It is likely then that at least one unique orientation of singly-derivatized pinonaldehyde sterically hinders the second carbonyl from derivatization. This is not surprising given the unique structure of the (S,S) conformation of carbons 1 and 3 in the butane ring of pinonaldehyde and many other α-pinene ozonolysis products. The designation of the ketonyl group of pinonaldehyde as the underivatized carbonyl was made due to the presence of a *m/z* 43 ion in the mass spectrum for the peaks at 24.8 and 25.3 min, corresponding to an acetyl fragment ($COCH_3$).

A similar phenomenon was found with the observed tricarbonyl product, oxopinonaldehyde, as peaks for both the doubly- and triply-derivatized compound were detected. In the literature, there is some discrepancy as to the identity of the α-pinene ozonolysis product with a molecular weight of 182 g/mol. It has been described as 4-oxopinonaldehyde (Yu et al. 2008), 10-oxopinonaldehyde (Kamens and Jaoui 2001), or both (Jaoui and Kamens 2003). Unfortunately, the mass spectra obtained do not show peaks that are specific to one isomer, so a definitive designation cannot be made. Formation pathways for both 4-oxopinonaldehyde and 10-oxopinonaldehyde from the ozonolysis of α-pinene, wherein an intermolecular reaction of two peroxyl radicals form the tricarbonyls, are proposed in Fig. 3.

3.3 Effects of cyclohexane addition and ·OH yields

Decomposition of the primary ozonide formed by alkene ozonolysis produces the Criegee intermediate. Further unimolecular decay of the Criegee intermediate may then lead to formation of OH radicals (Paulson and Orlando 1996). The ·OH yield from ozonolysis of α-pinene has been reported to be 68–91 % (Zhang and Zhang 2005; Atkinson and Arey 2003). As with O_3, ·OH can add to the carbon-carbon double bond of α-pinene and/or abstract

Table 1 Carbonyl-containing products observed from α-pinene ozonolysis

Compound	Retention Time (min)	Molecular structure	Molecular formula	Molecular Weight (g/mol)	Derivatized Molecular Weight (g/mol)	CI $[M+H]^+$ (m/z)	EI (m/z)	Yield w/ OH	Yield w/o OH
Glyoxal	15.3		$C_2H_2O_2$	58	200	201	57 (100) 88 (38) 41 (29) 144 (14)	1.7%	1.4%
Methylglyoxal	16.2		$C_3H_4O_2$	72	214	215	57 (100) 102 (90) 41 (34) 158 (22)	~1.5%[a]	~1.5%[a]
Pinonaldehyde	24.8[b] 25.3[b] 28.8 29.2 29.6 30.0		$C_{10}H_{16}O_2$	168	239[b] 310	240[b] 311	181 (100)[d] 254 (62) 57 (42) 85 (18)	76%	46%
Norpinonaldehyde	26.6 26.9		$C_9H_{12}O_2$	154	296	297	98 (100)[e] 57 (60) 84 (60) 111 (51)	2.0%	1.7%
Oxopinonaldehyde	33.3[c] 33.7[c] 35.6 35.8		$C_{10}H_{14}O_3$	182	324[b] 395	325[b] 396	266 (100)[f] 210 (51) 339 (27) 57 (21)	2.3%	7%
$C_{10}H_{16}O_4$	33.5	Unknown	$C_{10}H_{16}O_4$	200	342	343	57 (100) 41 (38) 213 (30) 154 (26)	< 1%	ND
Oxopinonic acid	35.3		$C_{10}H_{14}O_4$	198	340	340[g]	269 (100) 325 (79) 210 (56) 57 (50)	< 1%	ND

[a] Estimated yields due to peak overlap with an unknown compound

[b] Retention times and masses corresponding to singly-derivatized pinonaldehyde

[c] Retention times and masses corresponding to doubly-derivatized oxopinonaldehyde

[d] Specified ions and abundances for peak eluting at 29.2 min

[e] Specified ions and abundances for peak eluting at 26.9 min

[f] Specified ions and abundances for peak eluting at 35.8 min

[g] 340.2 m/z represents the [M]+ ion. An [M+H]+ ion was not observed for this compound

available hydrogens to generate oxygenated products. Furthermore, ·OH may react with ozonolysis products yielding second generation products. The addition of excess cyclohexane (283 ppm) to the reaction system effectively scavenges the OH radicals, preventing them from reacting with the terpene or ozonolysis products (Aschmann and Atkinson 1998). This allows for the determination of which oxidation products are formed solely from ozonolysis and which are formed from a combination of O_3 and ·OH.

Hydroxyl radical yields were estimated based on the cyclohexanone production from the ·OH initiated oxidation of cyclohexane, while employed as an ·OH scavenger. With the large concentration of cyclohexane, the formation of cyclohexanone is an indirect measure of the ·OH formation, since cyclohexane will scavenge the OH radicals. The cyclohexanone yield as a function of ozone concentration in this study is 26 % (Fig. S3). In order to derive the absolute values of the ·OH yield from the cyclohexanone yield, the branching ratio of the reaction ·OH + cyclohexane into cyclohexanone or cyclohexanol must be taken into account. For room temperature, this value has been reported to be approximately 0.5 (Atkinson et al. 1992; Berndt et al. 2003). Applying this ratio to the yield of cyclohexanone in this study, gives an ·OH yield of 52 %. When considering the mole balance under ·OH scavenging conditions, this value is

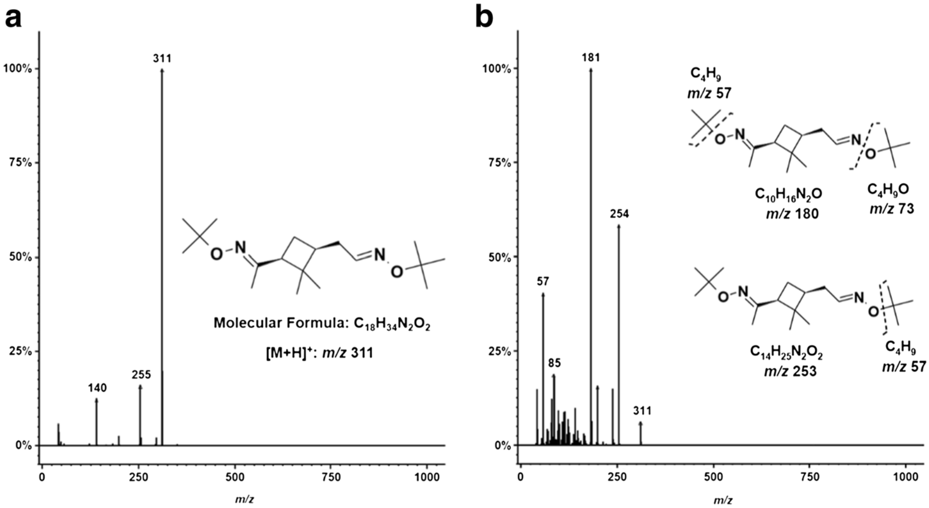


Fig. 1 CI **a** and EI **b** spectra for TBOX-derivatized pinonaldehyde. *m/z* 181 & 254 are likely a result of hydrogen rearrangement from a *t*-butyl group to the attached oxygen followed by adjacent cleavage (McLafferty and Tureček 1993)

consistent with the observed yield of pinonaldehyde in this study (46 %), since ·OH and pinonaldehyde put a mutual constraint on one another's formation (Tillmann et al. 2010).

In the presence of cyclohexane, the observed yield of pinonaldehyde decreased. This is unsurprising due to the existence of a pinonaldehyde formation pathway beginning with the ·OH-initiated oxidation of α-pinene (Eddingsaas et al. 2012). Simultaneously, ·OH may degrade pinonaldehyde to form smaller fragments of carbonyl compounds like CH_3CO, CH_2O, CH_2CHO, etc. (Fantechi et al. 2002; Grosjean et al. 1992); however, Hallquist et al. estimated the lifetime of pinonaldehyde to be a few hours with respect to ·OH, a reaction nearly five times slower than that of ·OH with α-pinene (Hallquist et al. 1997).

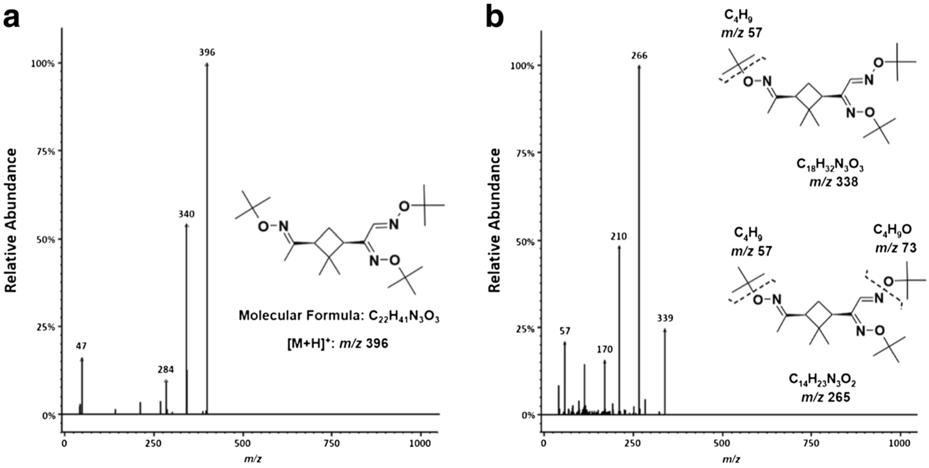


Fig. 2 CI **a** and EI **b** spectra for TBOX-derivatized oxopinonaldehyde. *m/z* 266 & 339 are likely a result of hydrogen rearrangement from a *t*-butyl group to the attached oxygen followed by adjacent cleavage (McLafferty and Tureček 1993)

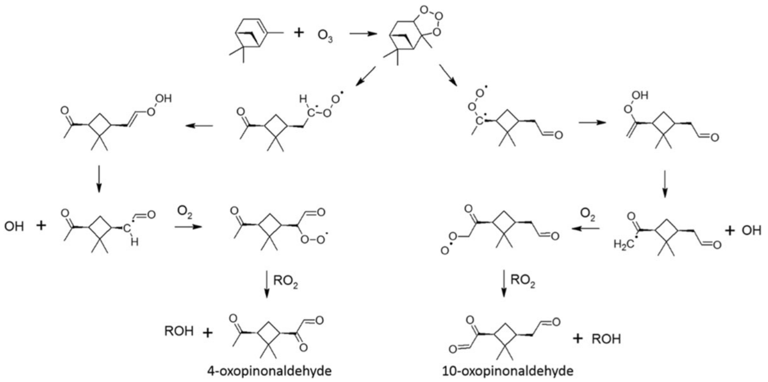


Fig. 3 Proposed formation pathways for 4-oxopinonaldehyde and 10-oxopinonaldehyde from the ozonolysis of α-pinene

3.4 Oxopinonaldehyde formation

Unlike pinonaldehyde, oxopinonaldehyde yields decrease when ·OH is present (7 % to 2.3 %). One possible cause for this is if ·OH reacts rapidly with oxopinonaldehyde or one of its precursors. Using AOPWIN v1.92 (EPA, 2000), the calculated overall oxopinonaldehyde/·OH rate constant is 1.83×10^{-11} cm^3 $molecules^{-1}$ s^{-1}. While fast, this calculated rate constant is not so fast that one would expect to see a nearly 70 % decrease in yield due to ·OH degradation of oxopinonaldehyde.

A more likely explanation is that the peroxyl radicals formed from the reaction of ·OH and cyclohexane aid in formation of oxopinonaldehyde. When cyclohexane is present to scavenge ·OH, a hydrogen is abstracted generating an alkyl radical, which then reacts in a diffusion-controlled manner with O_2 to produce a cyclohexylperoxyl radical (Atkinson 2003). In the proposed mechanisms shown in Fig. 3, the peroxyl radicals formed from α-pinene reacts with another peroxyl radical (i.e., cyclohexylperoxyl radicals), producing the tricarbonyl and an alcohol. This contribution to the pool of RO_2 radicals in the system allows for an increased chance for α-pinene-derived peroxyl radicals to react with another RO_2 radical instead of an alternative route. When cyclohexane is not present, ·OH will predominantly react by addition to excess α-pinene. While this reaction will produce peroxyl radicals as well, it has been found that the majority of these species will likely undergo H-shift or ring closure reactions which would lead to a decrease in the number of available peroxyl radicals (Vereecken et al. 2007; Eddingsaas et al. 2012).

To investigate this theory we used 2-butanol as an alternative ·OH scavenger. While the oxidation of cyclohexane exclusively produces RO_2 radicals, the major oxidation route of 2-butanol leads to the formation of HO_2 radicals and 2-butanone (Chew and Atkinson 1996). As a result, cyclohexane and 2-butanol have a different influence on the number of peroxyl radicals when used as ·OH radical scavengers, which ultimately has an influence on the product distribution from the ozonolysis of α-pinene (Jenkin 2004). This is shown by the chromatograms in Fig. 4, where the peaks for oxopinonaldehyde are largest when cyclohexane is used as an ·OH scavenger compared to 2-butanol or when there is no scavenger present.

It is also possible that oxopinonaldehyde is formed by degradation of the corresponding unstable hydroperoxide compound after being trapped in the aqueous medium. Recently Ehn et al. found evidence for highly oxygenated products from α-pinene ozonolysis in the gas-

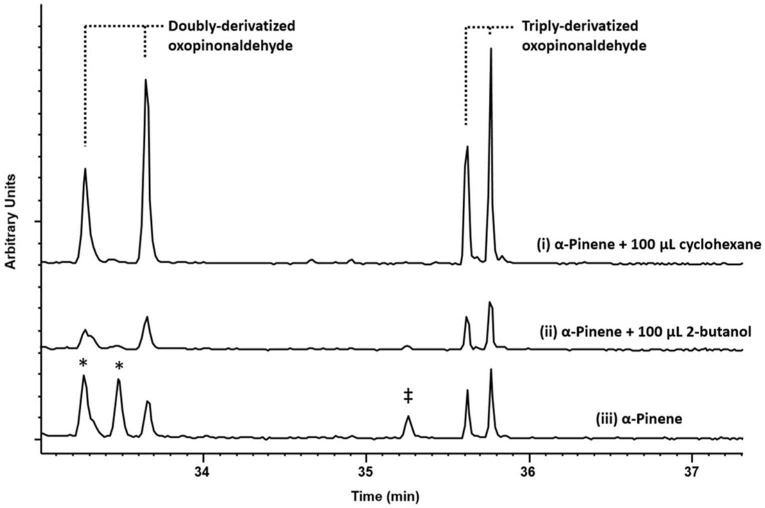


Fig. 4 Comparison of chromatogram peaks for oxopinonaldehyde when (i) a high-yield RO_2 producing scavenger is used (α-pinene +100 μL cyclohexane), (ii) a low-yield RO_2 producing scavenger is used (α-pinene +100 μL 2-butanol), and (iii) when no OH scavenger is used. * denotes peaks for $C_{10}H_{16}O_4$ while ‡ denotes the peak for oxopinonic acid. All chromatograms are presented on the same scale

phase that contain hydroperoxy groups (Ehn et al. 2014). In their suggested mechanism, the RO_2 formed upon ozonolysis would undergo intramolecular H-atom abstraction, followed by O_2 addition at the formed alkyl radical site, forming a hydroperoxide moiety and a new peroxy radical group on the C-atom where the hydrogen abstraction took place. While some of the observed oxopinonaldehyde may be formed this way, the decrease in yield observed when 2-butanol was used as a scavenger as opposed to cyclohexane suggests that a significant portion of the overall yield is likely produced by RO_2-RO_2 bimolecular reactions.

3.5 Comparisons with previous studies

Some studies have investigated oxidation products of α-pinene by using other carbonyl derivatization agents like *O*-(2,3,4,5,6-pentafluorobenyzl)hydroxylamine hydrochloride (PFBHA) (Jang 1999) or 2,4-dinitrophenylhydrazine (DNPH) (Van den Bergh et al. 2002). Derivatization often allows highly polar materials to be converted to thermally stable compounds so that they can be eluted at reasonable temperatures without decomposition or molecular rearrangement. In addition, derivatization methods are often very useful since identifying the number of specific functional groups on a molecule makes identification of the compound significantly easier, but steric hindrance and molecular mass play a very important role in the choice of the best suited derivatization reagent (Temime et al. 2007; Reisen et al. 2003). Many benchtop mass spectrometers have an upper *m/z* limit of 650, (Yinon 1991) but a tricarbonyl product like oxopinonaldehyde would have a molecular weight above that threshold when derivatized with PFBHA (767 g/mol for oxopinonaldehyde), making it difficult to detect with certain mass spectrometers.

Differences seen in the yield of OH radicals in our study compared to others' may be attributed to differences in oxidant concentrations. Along with ·OH, HO_2 may be formed during the multistep degradation of the Criegee intermediate (Nguyen et al. 2015). In studies that use large O_3 concentrations, HO_2 can then be converted to ·OH by O_3, giving rise to a higher yield of ·OH than observed in this study, using low O_3 concentrations (Atkinson et al. 2004; Jenkin 2004).

The pinonaldehyde yield found in this work (76 % w/ ·OH, 46 % w/o ·OH) is on the higher end of values reported in previous studies using a wide range of techniques (Hakola et al. 1994; Alvarado et al. 1998; Yu et al. 1999; Baker et al. 2002; Tillmann et al. 2010). This discrepancy could arise from a number of different sources. Most notably our experiments reflect the products in the presence of an abundance of α-pinene. Therefore it is not surprising that our values for pinonaldehyde yields are higher than reports where ozone and α-pinene are on the same order of magnitude (Warscheid and Hoffmann 2001; Ma et al. 2008; Yu et al. 1999), since there is a greater likelihood for ·OH to react with an α-pinene molecule yielding pinonaldehyde, versus reacting with pinonaldehyde or another ozonolysis product.

For the purposes of investigating chemistry occurring in the indoor environment, all experiments in this study were performed at 50 % RH. However, humidity has been suggested to influence both gas and particle-phase composition and distributions in the degradation of unsaturated compounds by O_3 (Bonn et al. 2002; Jonsson et al. 2006; von Hessberg et al. 2009; Wegener et al. 2007; Tillmann et al. 2010). The reported impact of RH varies significantly with regard to pinonaldehyde formation. Alvarado et al. suggested that the reaction of the stabilized Criegee Intermediate with water yielded pinonaldehyde under humid conditions (Alvarado et al. 1998). Warscheid and Hoffman reported an increase in pinonaldehyde yield with increased relative humidity (Warscheid and Hoffmann 2001) yet other studies have presented negative (Berndt et al. 2003) or neutral (Baker et al. 2002) dependence of pinonaldehyde production on water concentration.

Finally, these experiments were carried out under low NO_x conditions. At higher NO_x concentrations, additional reactions will likely be introduced into the system. If NO is present, it would react with O_3 to form NO_2 and O_2. OH radicals could also react with NO_2 to generate nitric acid. These reactions compete with the oxidants for α-pinene, which would decrease the yields for the ozonolysis products observed in this study. Future studies will study these reactions by adding varying concentrations of NO and NO_2 to the system, with an emphasis on detecting nitrogenated α-pinene oxidation products formed including nitrate esters and peroxyacyl nitrates.

4 Conclusion

Because of its large global emission, the oxidation mechanisms and resulting products of α-pinene have been a considerable focus of study. These efforts have led to the development of new analytical methods to explain the observed reaction products, some of which are designed with the indoor environment in mind, as ozonolysis of terpene compounds is a likely oxidation process indoors. The challenge of understanding this complex oxidation is the successful collection and identification of the oxidation products. Using a new derivatization technique, we identified and quantified a number of carbonyl-containing reaction products in the gas phase from the oxidation of α-pinene with O_3. Yields for individual products have been determined using the response factor of standards or similar reference compounds. Our findings show a high yield for pinonaldehyde from the oxidation of excess α-pinene with levels of ozone found indoors. The highly oxidized species oxopinonaldehyde was identified, and a formation pathway is proposed through a peroxyl radical precursor. Future investigations of α-pinene and other terpenes indoors using these techniques will provide for a better understanding of total exposures and their related health effects.

4.1 Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the Centers for Disease Control and Prevention/the Agency for Toxic Substances and Disease Registry. Mention of any commercial product or trade name does not constitute endorsement by the Centers for Disease Control and Prevention/NIOSH.

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