

## Use of denuder/filter apparatus to investigate terpene ozonolysis†

J. R. Wells\*

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A denuder/filter apparatus was used to collect the gaseous and particulate reaction products from ozonolysis of  $\alpha$ -pinene, limonene and  $\alpha$ -terpineol in an effort to develop sampling techniques for characterizing indoor environment chemistry. Carboxylic acids found in the particulate phase were derivatized to 2,2,2-trifluoroethylamides by reaction with 3-ethyl-1-[3-(dimethylamino)propyl] carbodiimide hydrochloride (EDC) and 2,2,2-trifluoroethylamine hydrochloride (TFEA). Carbonyl compounds collected in both gas phase and particulate phase were derivatized to their respective oximes by reaction with *O*-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine hydrochloride (PFBHA). The ozonolysis of  $\alpha$ -pinene yielded the carboxylic acids: *cis*-pinonic acid and pinic acid and the proposed carboxylic acids methanetricarboxylic acid and terpenylic acid; the carbonyls: 4-oxopentanal, norpinonaldehyde, pinon aldehyde and the proposed carbonyl methylidenepropanedial. The ozonolysis of limonene yielded the carboxylic acids: limonic acid and pinic acid and the carbonyls: 1-(4-methylcyclohex-3-en-1-yl)ethanone (4AMCH), glyoxal, methyl glyoxal, 4-oxopentanal and 6-oxo-3-(prop-1-en-2-yl)heptanal (IPOH). The ozonolysis of  $\alpha$ -terpineol yielded the proposed carboxylic acids: terpenylic acid and homoterpenylic acid and the carbonyls: (5*E*)-6-hydroxyhept-5-en-2-one, methyl glyoxal and 4-oxopentanal.

## Introduction

Consumer products such as cleaners can contain hundreds of compounds, and reactive terpenes such as limonene and  $\alpha$ -terpineol are in many formulations.<sup>1</sup> In indoor environments these and other terpenes can oxidize in the gas phase or on surfaces to form oxygenated organic species that could possibly lead to health effects.<sup>2–4</sup> Understanding the connection between indoor chemistry and health is an important component in effective prevention of illnesses such as work-related and/or work-exacerbated asthma. Unfortunately, no one specific chemical leading to negative health effects has been identified,

but the evidence continues to suggest that oxygenated organic compounds may play a role.<sup>5–9</sup> The connection between indoor environments and health effects is also supported by the epidemiological research results associating the use of cleaning products with exacerbation of occupational asthma.<sup>10–12</sup> To better understand and define indoor air quality, characterizing the link between indoor chemistry and health necessitates advancement in both chemical speciation and mechanistic toxicology.

In the indoor environment terpene oxidation reaction products can exist in the gas phase or contribute to the formation of particulate matter. The many reactions initiated by species such as ozone, hydroxyl radical (OH·) and nitrate radical (NO<sub>3</sub>·) transform terpenes into oxygenated organic compounds such as aldehydes, ketones, dicarbonyls, and organic acids.<sup>13–21</sup> Based on rate constant measurements of terpene/initiator reactions, terpene oxidation processes effectively compete with typical building air exchange, thereby establishing a need for accurate terpene oxidation mechanisms. While these processes are moderately well understood, the efficient collection and

Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Road, Morgantown, WV, 26505, USA. E-mail: ozw0@cdc.gov; Fax: +1-304-285-6041; Tel: +1-304-285-6341

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## Environmental impact

The use of simultaneous collection of particulate- and gas-phase terpene ozonolysis reaction products and two derivatization methods were used, coupled with standard gas chromatography/mass spectrometry, to characterize the carboxylic acids and carbonyls formed. Incorporation of these methods into routine indoor air sampling could improve the accuracy of occupant exposure assessment.

characterization of reaction product species are critical to verify proposed reaction mechanisms, improve indoor chemistry models, and ultimately define occupant exposures.

Recent efforts to determine carbonyl reaction product yields of terpene reactions anticipated in indoor environments has clearly shown that there are significant gaps in the carbon balance.<sup>22</sup> While it is likely that the “missing” carbon could be in aerosols, oxygenated reaction products other than carbonyls, or some high molecular weight oligomer, there is a major analytical challenge to characterize these different chemical species accurately and conveniently. Because many of the oxygenated organic species do not lend themselves to conventional detection, they usually must be transformed *via* derivatization to a less labile compound that can accommodate typical chromatographic parameters and temperatures.<sup>23,24</sup> While new analytical techniques have been developed to sample aerosols in near real time, a method that is simple to use yet sensitive and capable of collecting many different labile species would be an important advancement to improving the understanding of indoor air.<sup>25</sup>

Even though the chemistry of terpenes such as  $\alpha$ -pinene and limonene has been investigated for decades, insight into the dynamic nature of terpene oxidation continues to emerge and is needed by both the indoor and outdoor research communities.<sup>17,26,27</sup> Due to its significant presence in the atmosphere,  $\alpha$ -pinene's atmospheric oxidation has received considerable attention.<sup>28–35</sup> Identification of  $\alpha$ -pinene's gas-phase reaction products, both oxygenates and nitrates, has been used to propose reaction mechanisms that may also be applicable to other terpenes' oxidations.<sup>17,26,27,36</sup> Many of these mechanisms incorporate isomerization and molecular rearrangements yielding multi-carbonyl and multi-carboxylic acid species.<sup>17,26,27,36</sup> In addition to gas-phase species, significant effort has been expended to characterize not only the individual chemical components but also the chemical dynamics of aerosols formed from the  $\alpha$ -pinene reaction system.<sup>36–41</sup> Recent exploration of aerosol dynamics has demonstrated that the aging of oxygenated organic aerosol components results in the formation of acid and alcohol/peroxide functional group addition without C–C bond breakage and acid formation with C–C bond breakage.<sup>42</sup> Investigators of the particulate products of the  $\alpha$ -pinene system observed that additional oxidation, possibly through acid catalysis, of particulate components could lead to the formation of oligomers that can comprise over 50% of a particle's mass.<sup>36–41</sup> Recently, Hall and Johnston, investigating secondary organic aerosols' (SOA) solvent extraction methods, confirmed that more than 50% of the mass from particles formed in the  $\alpha$ -pinene system were oligomers.<sup>39</sup>

In order to better characterize indoor environments, the incorporation of new sampling and/or derivatization methods to capture terpene reaction products, both gas-phase and particle-phase, that are compatible with conventional analytical equipment would greatly benefit the industrial hygiene and exposure science communities. A significant advantage of a denuder/filter apparatus is the collection of gas-phase and particulate-phase species simultaneously and efficiently.<sup>43–47</sup> Applying different chemical derivatization techniques to the same sample is a practical approach to characterize the many oxidized species and different chemical classes likely present in the sample. This will ultimately improve understanding of indoor environment

exposure science. The novel part of this work is the simultaneous collection of gas and particle species and the use of more than one chemical derivatization technique to better characterize terpene oxidation in the indoor environment with an estimated sensitivity in the tens of part per billion.

The use of a denuder/filter collection system to capture both gas-phase and particulate-phase reaction products from the ozonolysis of three prominent terpenes,  $\alpha$ -pinene, limonene and  $\alpha$ -terpineol, will be presented here. The use of two chemical derivatization methods coupled with gas chromatography/mass spectrometry (GC-MS) was used to identify carboxylic acid and carbonyl reaction products. This is an improvement over using only one derivatization method or thermal desorption with denuder/filter sample collections which can hamper the ability to completely characterize indoor environments.<sup>43–48</sup> These three terpenes play significant roles in both the outdoor and indoor environments and an improved understanding of their reaction chemistry would benefit research in global climate and indoor air quality. Additionally, this is the first report of carboxylic reaction products from the  $\alpha$ -terpineol/ozone reaction system.

## Experimental section

### Apparatus and instruments

Methods to initiate terpene/ozonolysis reactions have been described previously.<sup>22</sup> A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4 mm Swagelok (Solon, OH) fitting attached to a 70 L Teflon-film chamber. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous  $\text{CaSO}_4$  (Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. The 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 of 50%. The filler system was equipped with a heated syringe injection port facilitating the introduction of liquid reactants into the chamber.

The reaction chamber was sampled for 3 min 20 s at a flow rate of  $18 \text{ L min}^{-1}$  (60 L total sample) onto a 5 channel, 400 mm length denuder (URG-2000-30B5, URG, Chapel Hill, NC) coated with ground XAD-4 resin (average particle size  $0.7 \mu\text{m}$ ) and a filter pack (URG-2000-30FG-3, URG, Chapel Hill, NC) with a 47 mm 0.45 micron PTFE filter (Fluoropore membrane, Millipore, Billerica, MA). The gaseous species diffuse to the denuder walls and are trapped while the particulate species exit the denuder (due to momentum) and deposit on the filter. Reaction products were analyzed as their oxime or 2,2,2-trifluoroethylamide derivatives, described below. A schematic of the experimental system is shown in Fig. 1.

All samples were then analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC-MS system operated in the electron ionization (EI) mode. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.25 mm I.D., 30 m long,  $1 \mu\text{m}$  film thickness) column and the following GC oven parameters:  $60^\circ\text{C}$  for 1 min., then  $20^\circ\text{C min}^{-1}$  to  $170^\circ\text{C}$ , then  $3^\circ\text{C min}^{-1}$  to  $280^\circ\text{C}$  and held for 5 min.  $1 \mu\text{L}$  of each sample was injected in the splitless mode, and the GC injector held at  $250^\circ\text{C}$  was returned

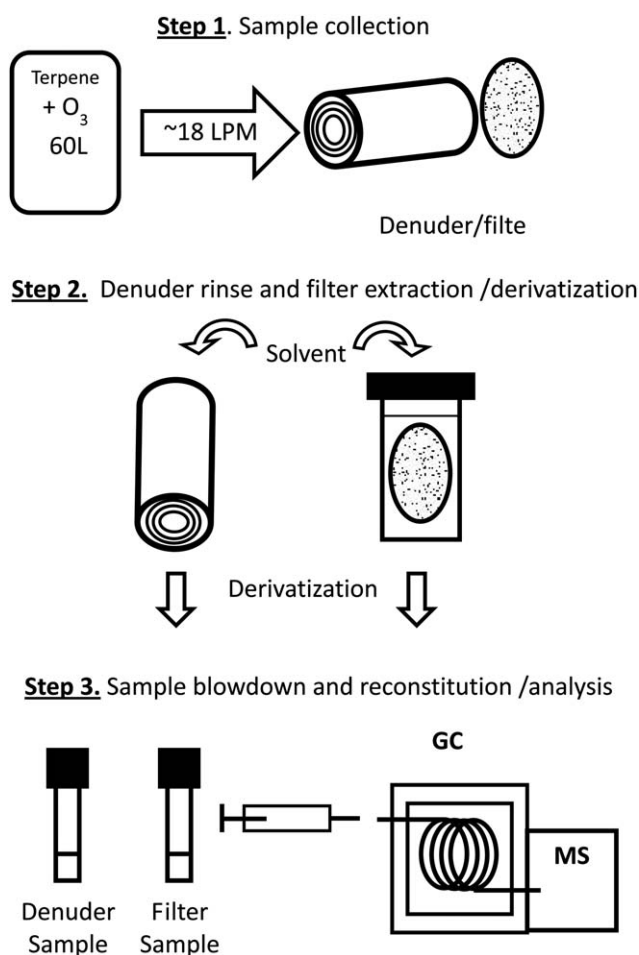


Fig. 1 Schematic of experimental method.

to split mode 1 min after sample injection. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI spectra were collected from  $m/z$  40–650. Each sample was analyzed in duplicate. Acetonitrile was the chemical ionization (CI) reagent used for all CI spectra. When possible, commercially available samples of the identified products were derivatized and subsequently analyzed to verify matching ion spectra and chromatographic retention times.

### Sample preparation and derivatization

After sampling, the denuder was extracted with 40 mL of CH<sub>2</sub>Cl<sub>2</sub> using a previously described technique.<sup>48,49</sup> This one extraction removed more than 95% of the collected reaction products. This is consistent with previously published work, and no carryover of carbonyl reaction products was observed in denuder extractions following the initial extraction.<sup>43</sup> To identify oxygenated reaction products (*i.e.*, aldehydes, ketones, and dicarbonyls), 400  $\mu$ L of *O*-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine hydrochloride (PFBHA) (20 mM in acetonitrile) was added to the methylene chloride extract. These vials were stored overnight for derivatization reaction completion. After reaction, the vials were blown down to approximately 4 mL, transferred and filtered into 4 mL vials then blown down to complete dryness using UHP N<sub>2</sub> then reconstituted in 100  $\mu$ L of methanol.<sup>22,24</sup>

After sampling, the filter was placed into a clean 40 mL vial and extracted, by shaking, with either 5 mL of deionized water (for carboxylic acid derivatization) or 5 mL of methylene chloride (for carbonyl derivatization). The carboxylic acid derivatization method by Ford *et al.* was slightly modified and used on the 5 mL deionized water extract.<sup>23</sup> Briefly, the water extract was placed in a 50 mL Erlenmeyer flask with 1 mL each of 0.4 M aqueous 3-ethyl-1-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) and 0.4 M aqueous 2,2,2-trifluoroethylamine hydrochloride (TFEA). This solution was stirred for 1 min then allowed to react for a minimum of 10 min. After reaction, this solution was transferred to a 25 mL separatory flask and 3 mL methyl *tert*-butyl ether (MTBE) was added. This mixture was vigorously shaken and the MTBE layer was collected into a 4 mL vial, blown to dryness with UHP N<sub>2</sub>, and reconstituted with 100  $\mu$ L of methanol. The carbonyl derivatization method for the methylene chloride filter extract is described above except 200  $\mu$ L of 20 mM PFBHA was used.<sup>24</sup>

### Chemicals and materials

Typical initial terpene ( $\alpha$ -pinene,  $\alpha$ -terpineol, limonene) concentrations in the reaction chamber were 2 ppm ( $5 \times 10^{13}$  molecules cm<sup>-3</sup>). Ozone (O<sub>3</sub>) was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon chamber and transferred using a gas-tight syringe. The ozone concentration was measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C. Typically, addition of O<sub>3</sub> resulted in an approximate final concentration of 0.4 ppm ( $9.8 \times 10^{12}$  molecules cm<sup>-3</sup>) in the terpene/air mixture. The gas-phase mixtures were allowed to react for at least 30 min after O<sub>3</sub> addition. In an effort to simulate indoor environments, no steps were taken to prevent secondary reactions such as between O<sub>3</sub> and reaction products formed or hydroxyl radical formation (OH·) but conditions were controlled to minimize side reactions. An O<sub>3</sub> concentration 20% of the terpene concentrations ensured O<sub>3</sub> was the limiting reagent.

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI):  $\alpha$ -pinene (98%), limonene (99%),  $\alpha$ -terpineol (90%, Technical Grade, however lot analysis from the manufacturer claims 99% purity), 3-Ethyl-1-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) (98%), 2,2,2-trifluoroethylamine hydrochloride (TFEA) (98%), methyl *tert*-butyl ether (MTBE) (99.8%), *O*-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine hydrochloride (PFBHA) (98+%), from Fisher Scientific (Fairlawn, NJ): methanol (HPLC grade), acetonitrile (ACN) (99.5%), XAD-4 resin. Water (DI H<sub>2</sub>O) was distilled, deionized to a resistivity of 18 M $\Omega$ ·cm and filtered using a Milli-Q® filter system (Billerica, MA). Helium (UHP grade), the GC carrier gas and nitrogen (UHP grade) were supplied by Amerigas (Sabraton, WV) and used as received. Experiments were carried out at  $297 \pm 3$  K.

### Results

The primary ozonide (POZ), formed upon O<sub>3</sub> addition to the terpene carbon-carbon double bond, subsequently reacts and/or rearranges to form oxygenated organic compounds such as carbonyls, dicarbonyls and carboxylic acids.<sup>21</sup> Very descriptive

reaction mechanisms for the ozonolysis of terpenes have been published elsewhere.<sup>21,26,50,51</sup>

The following chronological chromatographic retention time results and mass spectra data were observed utilizing EDC/TFEA and PFBHA derivatization and the Varian 3800/Saturn 2000 GC-MS system. The reaction products reported here were observed only after addition of O<sub>3</sub> to terpene/water/air. Derivatization experiments performed in the absence of O<sub>3</sub> but in the presence of all other chemicals in the reaction chamber did not result in any of the reaction products reported below. Aside from the positively identified reaction products with the synthesis of the derivatized oxime or 2,2,2-trifluoroethylamide compound, terpene/O<sub>3</sub> reaction product identification was derived from mass spectra data and previously published VOC/O<sub>3</sub> reaction mechanisms.<sup>13,52,53</sup> No carboxylic acids were identified in the background experiments while typically small amounts, of the carbonyls glyoxal and methyl glyoxal were observed in background experiments, based on peak area. The EDC/TFEA derivatization of the parent terpenes alone did not result in the observation of carboxylic acids.

Derivatization of carboxylic acids using EDC/TFEA resulted in a single chromatographic peak. Typically the 2,2,2-trifluoroethylamide compound (generic structure: F<sub>3</sub>CCH<sub>2</sub>NHC(=O)R) mass spectra included an ion between *m/z* 105–107 ([C(=O)NHCH<sub>2</sub>CF<sub>3</sub>]<sup>+</sup> fragment) which were used to generate extracted ion chromatograms.

Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes.<sup>24</sup> Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical. Typically, the PFBHA-derivatized oximes' mass spectra included an ion at *m/z* 181 ([CH<sub>2</sub>C<sub>6</sub>F<sub>3</sub>]<sup>+</sup> fragment) with a large relative intensity (>40%) and a [PFBHA oxime + 181]<sup>+</sup> ion (due to reactions in the ion trap mass spectrometer). In most cases, the *m/z* 181 ion relative intensity for the chromatographic peaks due to terpene + O<sub>3</sub> reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms.<sup>24</sup> Below are the data from the ozonolysis of  $\alpha$ -pinene, limonene,  $\alpha$ -terpineol, respectively. The values in parentheses after the ions are approximate relative signal intensities.

### $\alpha$ -Pinene + O<sub>3</sub>

Ozone adds to the lone double bond of  $\alpha$ -pinene to form a variety of oxygenated organic species.<sup>26,34,39,51,54</sup> The following paragraphs describe what was observed using the experimental collection and derivatization methods described above.

**14.6 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 14.6 min had ions of *m/z* 58 (100%), 72 (16%), 174 (14%). Using acetonitrile for chemical ionization an M + 1 ion of *m/z* of 392 was observed. Using the derivatized molecular weight of 148 for the triple 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 148. A proposed  $\alpha$ -pinene/O<sub>3</sub> reaction product assignment of methanetricarboxylic acid (see Table 1 and Fig. 2) was made based upon the observed data.

**14.8 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 14.8 min had ions of *m/z* 168 (28%), 83 (21%), 70 (17%), 58 (100%). Using acetonitrile for chemical ionization an M + 1 ion of *m/z* of 282 was observed. Assuming the doubly derivatized molecular weight of 281 for the 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 119. A proposed  $\alpha$ -pinene/O<sub>3</sub> reaction product assignment is challenging as the products that follow typical VOC reaction mechanisms have molecular weights of either 118 (methylpropanedioic acid) or 120 (hydroxypropanedioic acid).

**15.6 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 15.6 min had ions of *m/z* 266 (25%), 181 (13%), 154 (25%), 107 (16%), 106 (14%), 75 (100%), 58 (52%). Using acetonitrile for chemical ionization an M + 1 ion of *m/z* of 266 was observed. Using the derivatized molecular weight of 265 for the 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 184. A proposed  $\alpha$ -pinene/O<sub>3</sub> reaction product assignment of *cis*-pinonic acid (see Table 1) was made based upon the observed data and comparison with derivatized *cis*-pinonic acid standard.<sup>34,54</sup>

**17.7 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 17.7 min had ions of *m/z* 167 (24%), 106 (15%), 139 (13%). Using acetonitrile for chemical ionization an M + 1 ion of *m/z* of 254 was observed. Using the derivatized molecular weight of 253 for the 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 172. A proposed  $\alpha$ -pinene/O<sub>3</sub> reaction product assignment of (2,2-dimethyl-5-oxotetrahydrofuran-3-yl) acetic acid (terpenylic acid) (see Table 1 and Fig. 3) was made based upon the observed data. This has been observed in the literature of  $\alpha$ -pinene ozonolysis.<sup>26,51</sup>

**19.25 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 19.3 min had ions of *m/z* 349 (15%), 249 (30%), 208 (30%), 195 (55%), 181 (100%), 106 (75%), 83 (100%), 69 (35%), 55 (75%). Using acetonitrile for chemical ionization an M + 1 ion of *m/z* of 349 was observed. Using the derivatized molecular weight of 348 for the doubly derivatized 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 186. A proposed  $\alpha$ -pinene/O<sub>3</sub> reaction product assignment of pinic acid (see Table 1) was made based upon the observed data and previous research.<sup>26,34,51,54</sup>

Similar to previous PFBHA data there are typically multiple peaks for each single compound because of the many different molecular orientations for the same derivatized molecule. The incorporation of mass spectral data is used to verify that peaks with chromatographically similar retention times are the same reaction product. Some carbonyls observed from these experiments have been previously identified by this and other research groups: 4-oxopentanal, 2,2-dimethyl-3-(2-oxoethyl) cyclobutanecarbaldehyde or norpinonaldehyde, 3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde or pinon aldehyde.<sup>20,22,24,34,54–57</sup> Norpinonaldehyde and pinon aldehyde were both observed in the PFBHA analysis of particulate matter samples.

**Table 1** Selected reaction products observed from  $\alpha$ -pinene ozonolysis


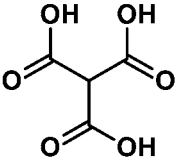
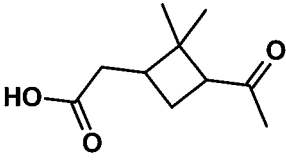
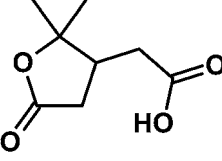
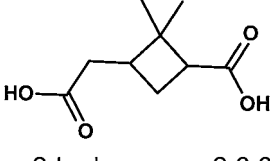
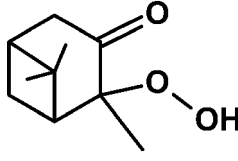
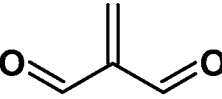
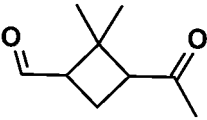
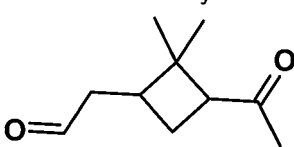
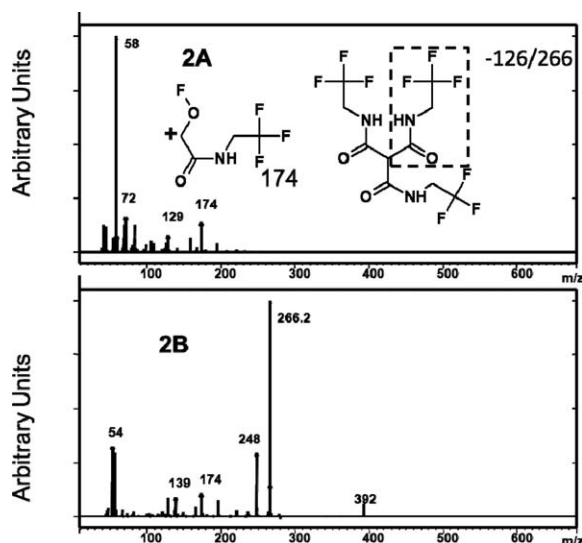
Product name structure	Molecular weight (g mol <sup>-1</sup> )	<i>m/z</i> (Acetonitrile-Cl) derivatives	Particulate phase? Yes = X
$\alpha$ -Pinene 	136		
methanetricarboxylic acid 	148	392	X
cis-pinonic acid 	184	266	X
Terpenylic acid 	172	254	X
pinic acid 	186	349	X
2-hydroperoxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one 	184	380	
methylidenepropanedial 	84	475	
Norpinon aldehyde 	154	545	X



Table 1 (Contd.)

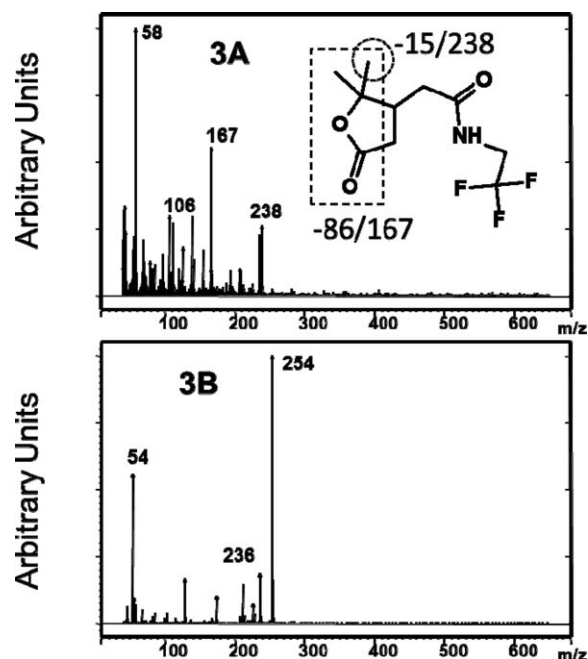
Product name structure	Molecular weight (g mol <sup>-1</sup> )	<i>m/z</i> (Acetonitrile-CI) derivatives	Particulate phase? Yes = X
<p>Pinon aldehyde</p> 	168	559	X



**Fig. 2** 2,2,2-Trifluoroethylamide derivative observed at retention time of 14.6 min: methanetricarboxylic acid. 2A is the EI spectrum and 2B is the CI spectrum. Dashed lines on molecular structure indicate fragmentation.

**22.5 min.** The oxime observed with chromatographic peak at retention time of 22.5 min had ions of *m/z* 181 (100%), 122 (79%), 346 (63%), 320 (31%). Using acetonitrile for chemical ionization an *M* + 1 ion of *m/z* of 346 was observed. Using the derivatized molecular weight of 345 for the oxime suggests a carbonyl compound with a molecular weight of 150. A proposed  $\alpha$ -pinene/*O*<sub>3</sub> reaction product assignment is not definitive due to the possibility of several structures: 1-(6-methylcyclohexa-1,3-dien-1-yl)propan-2-one, 3-ethenylidene-2,2-dimethylcyclobutyl) acetaldehyde or 1-(3-ethenylidene-2,2 dimethylcyclobutyl) ethanone.

**22.6 min.** The oxime observed with chromatographic peak at retention time of 22.6 min had ions of *m/z* 181 (100%), 264 (69%). Using acetonitrile for chemical ionization an *M* + 1 ion of *m/z* of 279 was observed. Using the derivatized molecular weight of 278 for the oxime suggests a carbonyl compound with a molecular weight of 83. A proposed  $\alpha$ -pinene/*O*<sub>3</sub> reaction product assignment is challenging as the products that follow typical VOC reaction mechanisms have molecular weights of either 82 (2-methylidenecyclobutanone) or 84 (pent-1-en-1-one).



**Fig. 3** 2,2,2-Trifluoroethylamide derivative observed at retention time of 17.7 min: terpenylic acid. 3A is the EI spectrum and 3B is the CI spectrum. Dashed lines on molecular structure indicate fragmentation.

**23 min.** The oxime observed with chromatographic peak at retention time of 22.6 min had ions of *m/z* 181(100%), 264 (69%), 198 (60%), 152 (49%). Using acetonitrile for chemical ionization an *M* + 1 ion of *m/z* of 380 was observed. Using the derivatized molecular weight of 379 for the oxime suggests a carbonyl compound with a molecular weight of 184. A proposed  $\alpha$ -pinene/*O*<sub>3</sub> reaction product assignment of 2-hydroperoxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (see Table 1) was made based upon the observed data.

**24.9 and 25.7 min.** The oxime observed with chromatographic peaks at retention times of 24.9 and 25.7 min had ions of *m/z* 264 (100%), 181 (83%), 320 (28%). Using acetonitrile for chemical ionization an *M* + 1 ion of *m/z* of 361 was observed. Using the derivatized molecular weight of 360 for the oxime suggests a carbonyl compound with a molecular weight of 165. A proposed  $\alpha$ -pinene/*O*<sub>3</sub> reaction product assignment is not conclusive and a reasonable structure of molecular weight 164 of 3-(1-hydroxyethenyl)-4,4-dimethylcyclobut-2-en-1-ylidene]acetaldehyde was proposed based upon the observed data. This

product was also observed in the PFBHA analysis of particulate matter captured on filters.

**32.3, 32.7 min.** The oxime observed with chromatographic peaks at retention times of 32.7, 33.2 min had ions of  $m/z$  181 (100%), 250 (18%), 223 (17%), 263 (17%), 292 (12%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 475 was observed. Using the doubly derivatized molecular weight of 474 for the oxime suggests a carbonyl compound with a molecular weight of 84. A proposed  $\alpha$ -pinene/ $O_3$  reaction product assignment of methylenepropenedial (see Table 1 and Fig. 4) was made based upon the observed data.

**39.9, 40.3, 40.5, 40.9 min.** The oxime observed with chromatographic peaks at retention times of 39.9, 40.3, 40.5, 40.9 min had ions of  $m/z$  361 (100%), 181 (78%), 94 (46%), 377 (43%), 264 (36%), 266 (34%), 112 (24%), 67 (22%), 362 (20%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 559 was observed. Using the doubly derivatized molecular weight of 558 for the oxime suggests a carbonyl compound with a molecular weight of 168. A proposed  $\alpha$ -pinene/ $O_3$  reaction product assignment of (3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde or pinon aldehyde (see Table 1) was made based upon the observed data and published literature.<sup>24,34,54,56,57</sup> This product was also observed in the PFBHA analysis of particulate matter captured on filters.

### Limonene + $O_3$

Ozone adds to the two double bonds of limonene to form a variety of oxygenated organic species.<sup>58,59</sup> The following

paragraphs describe what was observed using the experimental collection and derivatization methods described above.

**14.4 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 14.4 min had ions of  $m/z$  43 (100%), 141 (56%), 208 (49%), 106 (46%), 232 (41%), 166 (35%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 266 was observed. Using the derivatized molecular weight of 265 for the doubly derivatized 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 184. A proposed limonene/ $O_3$  reaction product assignment of 6-oxo-3-(prop-1-en-2-yl)heptanoic acid (Limonic acid) (see Table 2) was made based upon the observed data.<sup>58,59</sup>

**19.5 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 16 min had ions of  $m/z$  249 (100%), 106 (96%), 208 (68%), 195 (60%), 281 (52%), 221 (45%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 349 was observed. Using the derivatized molecular weight of 348 for the doubly derivatized 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 186 for double derivatization. A proposed limonene/ $O_3$  reaction product assignment of pinic acid (see Table 2) was made based upon the observed data and comparison with  $\alpha$ -pinene ozonolysis data above.

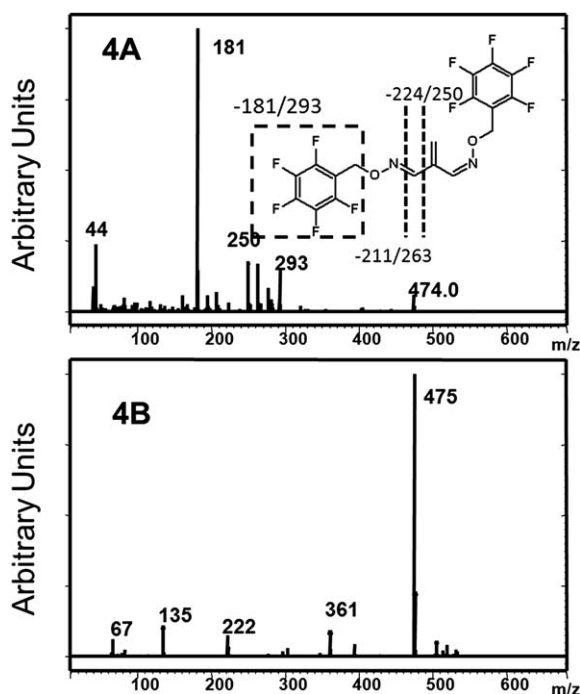
The three carbonyls observed in this series of experiments are the same three that have been observed previously by this and other research groups: 1-(4-methylcyclohex-3-en-1-yl)ethanone (4AMCH), glyoxal, methyl glyoxal, 4-oxopentanal and 6-oxo-3-(prop-1-en-2-yl)heptanal (IPOH). The mass spectrometer analysis can be found elsewhere.<sup>22,58,59</sup>

### $\alpha$ -Terpineol + $O_3$

Ozone adds to the lone double bond in  $\alpha$ -terpineol to form a variety of oxygenated organic species. The following paragraphs describe what was observed using the experimental collection and derivatization methods described above.

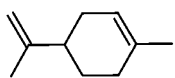
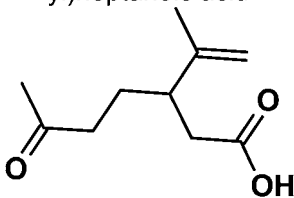
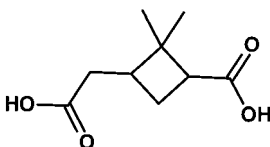
**17.7 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 17.7 min had ions of  $m/z$  167 (24%), 106 (15%), 139 (13%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 254 was observed. Using the derivatized molecular weight of 253 for the 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 172. A proposed  $\alpha$ -terpineol/ $O_3$  reaction product assignment of (2,2-dimethyl-5-oxotetrahydrofuran-3-yl)acetic acid (terpenylic acid) (see Table 3) was made based upon the observed data. This has been observed in the literature of  $\alpha$ -pinene ozonolysis.<sup>26,51</sup>

**21 min.** The 2,2,2-trifluoroethylamide derivative observed with chromatographic peak at retention time of 21 min had ions of  $m/z$  181 (100%), 141 (65%), 249 (49%), 106 (44%). Using acetonitrile for chemical ionization an  $M + 1$  ion of  $m/z$  of 268 was observed. Using the derivatized molecular weight of 267 for the 2,2,2-trifluoroethylamide derivative suggests a carboxylic acid compound with a molecular weight of 186. A proposed  $\alpha$ -terpineol/ $O_3$

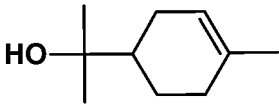
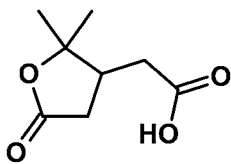
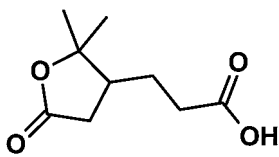


**Fig. 4** PFBHA oxime derivative observed at retention time of 32.3 min: methylenepropenedial. 4A is the EI spectrum and 4B is the CI spectrum. Dashed lines on molecular structure indicate fragmentation.

**Table 2** Selected reaction products observed from limonene ozonolysis

Product name structure	Molecular weight (g mol <sup>-1</sup> )	<i>m/z</i> (Acetonitrile-Cl) derivatives	Particulate phase? Yes = X
<b>Limonene</b> 	136		
<b>6-oxo-3-(prop-1-en-2-yl)heptanoic acid</b> 	184	266	X
<b>pinic acid</b> 	186	349	X

**Table 3** Selected reaction products observed from  $\alpha$ -terpineol ozonolysis

Product name structure	Molecular weight (g mol <sup>-1</sup> )	<i>m/z</i> (Acetonitrile-Cl) derivatives	Particulate phase? Yes = X
<b><math>\alpha</math>-Terpineol</b> 	154		
<b>Terpenylic acid</b> 	172	254	X
<b>Homoterpenylic acid</b> 	186	268	X

reaction product assignment of 3-(2,2-dimethyl-5-oxotetrahydrofuran-3-yl)propanoic acid (homoterpenylic acid) (see Table 3) was made based upon the observed data. This has been observed in the literature of  $\alpha$ -pinene ozonolysis.<sup>26,51</sup>

The three carbonyls observed in this series of experiments are the same three that have been observed previously by this group: (5*E*)-6-hydroxyhept-5-en-2-one, methyl glyoxal and 4-

oxopentanal. The mass spectrometer analysis can be found elsewhere.<sup>20,22</sup>

## Discussion

The ozonolysis of terpene compounds is a likely oxidation process in the indoor environment.<sup>21,60–62</sup> The challenge of understanding this complex oxidation is the successful collection



and identification of the oxidation products. While simple in theory this task is complicated because these reaction products can be both in the gas and/or particulate phases, the potential reaction products encompass a wide variety of structures (carbonyls, carboxylic acids, hydroperoxides, *etc.*), and many analytical methods lead to reaction product decomposition and subsequent non-detection. The simultaneous collection of gas-phase and particle-phase carbonyls has been used to investigate the outdoor environment.<sup>44</sup> New analytical equipment has been recently developed to collect aerosols.<sup>25</sup> However, the work presented here is one of the few to report the collection and characterization of both carboxylic acid and carbonyl reaction products simultaneously.

While the initial terpene and ozone concentrations were elevated at 2 ppm and 0.4 ppm, respectively, the fact that products were observed data from the relatively small sample volume (60 L) certainly implies the method's potential practicality for field measurements.

### $\alpha$ -Pinene

As a major biogenic emission,  $\alpha$ -pinene and its subsequent oxidation has been the subject of many research efforts emphasizing secondary organic aerosol (SOA) formation.<sup>26,39,51</sup> These efforts have led to the development of new reaction mechanisms as well as analytical methods to explain the observed reaction products.<sup>26,51</sup> Many molecular rearrangements resulting in higher molecular weight low vapor pressure oxygenated organic compounds are proposed. Briefly, these compounds can be the result of decomposition of the POZ and/or the additional side reaction between the  $\alpha$ -pinene ozonolysis reaction product and the hydroxyl radical ( $\text{OH}\cdot$ ).<sup>63–66</sup> The reaction mechanisms for some of the reaction products can be found in greater detail elsewhere.<sup>24,26,39,51,67,68</sup> The observation of both *cis*-pinonic and pinic acids from the experimental system is expected as they have been observed in previous literature.<sup>34,54</sup>

Of the carboxylic acids, the mechanism of formation of terpenylic acid (Table 1 and Fig. 3) highlights the  $\text{OH}\cdot$  role.<sup>26,51</sup> Identification of this compound was aided by the use of chemical ionization. In Fig. 3b the  $M + 1$  mass of 254 is evident in the chemical ionization spectrum, but not in the electron impact ionization spectrum (Fig. 3a). In the electron impact spectrum the loss of the  $[\text{CH}_3]$  fragment yields the  $m/z$  238 ion, while the loss of  $[\text{C}(=\text{O})\text{OC}(\text{CH}_3)_2]$  could result in the  $m/z$  167 ion.

However, one unusual proposed product was observed as a result of  $\alpha$ -pinene ozonolysis: methanetricarboxylic acid. Identification of this tricarboxylic acid would have been difficult, if not impossible, without the use of chemical ionization. In Fig. 2b the  $M + 1$  mass of 392 is evident in the chemical ionization spectrum, but not in the electron impact ionization spectrum (Fig. 2a). The loss of the  $[\text{C}(=\text{O})\text{NHCH}_2\text{CF}_3]$  fragment gives the  $m/z$  266 ion. While this reaction product has not been previously observed, a reasonable formation mechanism from three sided molecular decomposition and either of the bridging carbons at the "points" of the cyclobutane moiety could be the center carbon of methanetricarboxylic acid.

Most of the carbonyl compounds observed from this investigation are for the most part consistent with previously published results.<sup>34,54</sup> However, the observation of the dicarbonyl

methylidenepropanedial (Table 1 and Fig. 4) is reported for the first time. Again, the use of chemical ionization coupled with electron ionization mass spectrometry and chemical derivatization was essential to propose this reaction product.

While some of the lower molecular weight gas-phase carbonyl compounds were not observed in the particulate phase, the higher molecular weight carbonyls were present in both gas and particulate-phase. It should be noted that there were no particulate carbonyls that were not present in the gas-phase suggesting that additional particulate chemistry is not likely.

### Limonene

Similar to  $\alpha$ -pinene, the reaction products of limonene ozonolysis have been investigated in order to understand SOA formation and characterization.<sup>58,59,69</sup> The observation of limonic acid in the results reported here are consistent with previous work. However, the unexpected observation of pinic acid suggests that some molecular rearrangement occurs to bridge the *exo*-carbon-carbon double bond forming the cyclobutane moiety rather than further decomposition. Contrasting this mechanism with the formation of terpenylic acid for  $\alpha$ -pinene, it is not unexpected for this type of ring closure.<sup>51</sup> The observation of pinic acid is not likely due to  $\alpha$ -pinene contamination, because none of the  $\alpha$ -pinene carbonyl products were observed in the PFBHA derivatization of the limonene/ $\text{O}_3$  reaction.

The carbonyl compounds observed were consistent with literature and typical VOC/ $\text{O}_3$  mechanisms.<sup>58,59,69</sup> Also like  $\alpha$ -pinene, some of the lower molecular weight gas-phase carbonyl compounds were not observed in the particulate phase, the higher molecular weight carbonyls were present in both gas and particulate-phase.

### $\alpha$ -Terpineol

This is the first report of carboxylic acid reaction products for the  $\alpha$ -terpineol ozonolysis. The mechanisms of terpenylic acid and homoterpenylic acid formation likely have similar paths to the previously proposed  $\alpha$ -pinene mechanism.<sup>26,51</sup> Again the observation of these compounds clearly demonstrate the molecular rearrangements that take place leading to the formation of products. The gas-phase carbonyl compounds have been reported previously, however, none were observed in the particulate phase most likely due to their lower molecular weight.

### Method

The combined denuder/filter method with the added benefit of derivatization allows for improved characterization of terpene ozonolysis reaction products. Importantly the sampling flow rate can be used to "tune" the denuder for particle sizes of interest. Under the experimental conditions used here the denuder effectively removed gases and allowed over half of the particles with an aerodynamic diameter of 6 nm to pass through to the filter while particles with an aerodynamic diameter of 1 nm or less diffuse to the denuder walls. The denuder's ability to trap particles drops dramatically for particles with an aerodynamic diameter of 30 nm or greater and a decrease of almost 20% between 10 nm and 20 nm aerodynamic diameter particles.<sup>49</sup> Future plans include using the denuder/filter apparatus to

determine reaction product yields from terpene ozonolysis reactions, both single terpene and terpene mixtures, and conduct field measurements.

## Conclusions

The use of a denuder to capture gas-phase species and filter for particulate-phase species coupled with chemical derivatization is a promising avenue to address the many questions of indoor environment chemistry and occupant exposure. The methods for this investigation were chosen based on practicality for use in industrial hygiene, minimal sample preparation, and sensitivity. The advantage of the EDC/TFEA technique is the use of water to extract the filters which avoids taking large volumes of solvent in field sampling campaigns. Future work will include detailed exploration of analytical optimization and investigations of other terpene/ozone and mixed terpene/ozone reaction systems.

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