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Investigation of terpinolene + ozone or terpinolene + nitrate radical reaction products using denuder/filter apparatus

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HIGHLIGHTS

- Determined and contrasted the products of the reaction of terpinolene with ozone or nitrate radical.
- Products captured using a denuder/filter apparatus.
- Reaction products identified using a dual derivatization method.

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ABSTRACT

Terpinolene's (1-methyl-4-(propan-2-ylidene)cyclohexene) reaction with ozone or the nitrate radical was investigated using a denuder/filter apparatus in order to characterize gas-phase and particulate reaction products. Identification of the reaction products (i.e., aldehydes, ketones, dicarbonyls and carboxylic acids) was made using two derivatization methods; *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to derivatize the carbonyl products or 3-Ethyl-1-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) and 2,2,2-trifluoroethylamine hydrochloride (TFEA) to derivatize the carboxylic acid products. Proposed carbonyl products for ozonolysis of terpinolene are: 4-methylcyclohex-3-en-1-one, 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal, methyl glyoxal, 3-oxobutanal, and 6-oxo-3-(propan-2-ylidene)heptanal. Proposed carbonyl products for nitrate radical reaction of terpinolene are: 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal, methyl glyoxal, and 4-oxopentanal. No carboxylic acid products were detected with either oxidizing reactant.

1. Introduction

Volatile organic compounds (VOCs) are introduced indoors by outdoor ventilation, emissions from building materials, and the use of various cleaning products (Nazaroff and Weschler, 2004). In indoor environments these VOCs can react with oxidants such as ozone (O_3) and the nitrate radical (NO_3•) in the gas phase or on indoor surfaces and can transform into oxygenated organic and/or nitrated species. Indoors the reaction of ozone and NO_2 yields nitrate radicals (NO_3•) with an estimated concentration of 2×10^7 molecules cm^{-3} (1.1 parts per trillion) (ppt) (Sarwar et al., 2002). An indoor ozone concentration of 1×10^{12} molecules cm^{-3} (50 parts per billion) (ppb) has been estimated by Sarwar et al. (2002). Using these concentration estimates in combination with VOC/ozone or VOC/nitrate radial reaction rate constants, VOC removal rates due to reaction effectively competes with typical indoor air exchange (0.6 h^{-1}) (Wilson et al., 1996). Thus, identifying the VOC/O_3 and VOC/NO_3• reaction products for VOC typically present indoors is critical to characterize occupant exposure (Quirce and Barranco, 2010; Makela et al., 2011; McHugh et al., 2010).

The VOC/O_3 and VOC/NO_3• reaction products for VOC normally found indoors encompass a wide variety of oxygenated organic compounds. These reactions proceed by addition to carbon–carbon double bonds and also by H abstraction for VOC/NO_3• reactions. The reaction products formed include: aldehydes, ketones, dicarbonyls, carboxylic acids, and organic nitrates (e.g. alkyl nitrates, peroxyacyl nitrates (PANs), hydroxynitrates, dinitrates) (Atkinson and Arey, 2003; Spittler et al., 2006; Wangberg et al., 1997). It is expected that many of these compounds may have harmful health effects and should be investigated. All of these oxygenated organic compounds have the potential to induce a respiratory response, including WRA (Magnano et al., 2009). Organic nitrates may also have the potential to be carcinogenic (Dungworth et al., 1969). Determining the reaction products of NO_3• and O_3 reactions

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with VOC are essential in assessing potential exposures of indoor occupants.

One VOC common in many cleaning formulations is terpinolene (1-methyl-4-(propan-2-ylidene)cyclohexene). Recent work by Singer et al. determined the 1 h concentration of terpinolene after the application of a full strength cleaning product to be 900–1300 μg m^{-3} (~160–230 ppb) (Singer et al., 2006). Terpinolene with its two carbon–carbon double bonds reacts rapidly with O_3 or NO_3• with rate constants (in units of cm^3 $molecule^{-1}$ s^{-1}) of 190×10^{-17} and 97×10^{-12}, respectively (Atkinson and Arey, 2003). More recently Stewart et al. (2013) published recommended values for rate constants of terpinolene reaction with O_3 or NO_3• (in units of cm^3 $molecule^{-1}$ s^{-1}) of 154×10^{-17} and 50×10^{-12}, respectively. Previous investigations of terpinolene oxidation chemistry include: three from terpinolene/ozone (Ma and Marston, 2009;Reissell et al., 1999; Hakola et al., 1994) and one from terpinolene/nitrate radical reaction product kinetics (Baker et al., 2004). In this present study, the oxidation of terpinolene due to reaction with ozone or nitrate radical was investigated using a denuder/filter apparatus to characterize gas-phase and particulate reaction products. Identification of the reaction products (i.e., aldehydes, ketones, dicarbonyls, and carboxylic acids) was made using two derivatization methods: *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to derivatize the carbonyl products (Yu et al., 1998) or 3-Ethyl-1-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) and 2,2,2-trifluoroethylamine hydrochloride (TFEA) to derivatize the carboxylic acid products (Ford et al., 2007).

2. Experimental methods

2.1. Apparatus and materials

Experiments to measure the gas-phase reaction products formed from the reaction of terpinolene with O_3 or NO_3• were conducted with a previously described apparatus (Harrison et al., 2007). 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 95 L Teflon-film chamber. 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 of 50%. The filler system was equipped with a heated syringe injection port facilitating the introduction of liquid reactants into the chamber. All reactant mixtures and calibration standards were generated by this system.

Identification of reaction products was made using PFBHA to derivatize carbonyl products or EDC and TFEA to derivatize carboxylic acid products. Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in both the electron ionization (EI) and chemical ionization (CI) modes (Yu et al., 1998). Compound separation was achieved by a Restek (Bellefonte, PA) RTX-5MS (0.25 mm i.d., 30-m long, 1 μm film thickness) column and the following gas chromatograph (GC) oven parameters: 40 °C for 2 min then 10 °C min^{-1} to 140 °C, then 20 °C min^{-1} to 280 °C and held for 8 min.

Samples were injected in the splitless mode, and the GC injector was returned to 50:1 split mode one minute after sample injection, with the following injector temperature parameters: 200 °C for 0.5 min then 200 °C min^{-1} to 300 °C and held for 6 min. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI spectra were collected from *m/z* 40 to 650. Acetonitrile was the 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.

Ozone was produced by photolyzing air with a mercury pen lamp in a separate Teflon chamber. Aliquots of this O_3/air mixture were added to the Teflon reaction chamber using a gas-tight syringe. O_3 concentrations were measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C.

Nitrate radicals (Reaction 1) were generated by the thermal decomposition of N_2O_5 using a similar method as described by Atkinson et al. (1988). N_2O_5 (solid) kept at −75 °C was heated and allowed to transfer to an evacuated 2 L collection bottle until pressure was between 0.1 and 0.2 Torr. The collection bottle was then pressurized with ultra-high purity nitrogen up to 1000 Torr and connected to the reaction chamber via a Teflon® shut-off valve. The valve to the collection bottle and the chamber shut-off valve were opened and the system was allowed to equilibrate for 20 s. For product experiments, approximately 30 min elapsed before any samples were collected after the introduction of ozone or N_2O_5.

$$N_2O_5 \overset{M}{\rightleftarrows} NO_3^{\bullet} + NO_2 \qquad (1)$$

All compounds were used as received and had the following purities: from Sigma–Aldrich (Milwaukee, WI): Terpinolene (90%), methylene chloride (99.5%) 3-Ethyl-1-[3-(dimethylamino)propyl] carbodiimide hydrochloride (EDC) (98%), 2,2,2-trifluoroethylamine hydrochloride (TFEA) (98%), O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) (98+%), from Fisher Scientific (Fairlawn, NJ): acetonitrile (ACN) (99.5%), XAD-4 resin and methanol (99%). Water (DI H_2O) was distilled, deionized to a resistivity of 18 MΩ cm and filtered using a Milli-Q® filter system (Billerica, MA). Nitrogen dioxide as a 5% mixture in nitrogen and ultra-high purity (UHP) oxygen was obtained from Butler Gases (Morrisville, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV) and used as received. Experiments were carried out at (297 ± 3) K and 1 atm pressure.

2.2. Experimental procedures and sample derivatization

For the terpinolene + O_3 or NO_3• experiments, the typical concentrations of the terpinolene in the 95 L Teflon chamber were 1 ppm (2.5×10^{13} molecule cm^{-3}), 0.1 ppm (2.5×10^{12} molecule cm^{-3}) of ozone, or 0.2 ppm (5×10^{12} molecule cm^{-3}) of NO_3•. All solutions were added through the syringe injection port (described above). An additional port attached to the Teflon chamber enabled the injection of N_2O_5 or O_3. After terpinolene was injected, background samples were taken before addition of O_3 or NO_3•. All sample collections (described below) were treated the same. Each experiment was conducted at least three times.

The reaction chamber was sampled for 3 min 20 s at a flow rate of 18 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 mm) 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-trifuoroethylamide derivatives, described below.

After sampling, the denuder was extracted with 30 mL of methylene chloride using a previously described method (Wells, 2012). To identify oxygenated reaction products (i.e., aldehydes, ketones, and dicarbonyls), 100 μL of PFBHA (Yu et al., 1998) (250 mM in deionized H_2O) was added to the methylene chloride extract. These vials were stored overnight for derivatization reaction completion. After reaction, the deionized water layer was carefully removed and the remaining methylene chloride extract in the vials were blown down to approximately 6 mL, transferred into 7 mL vials then blown down to complete dryness using dry house air and then reconstituted in 100 μL of methanol.

After sampling, the filter was placed into a clean 40 mL vial and extracted, by shaking, with 5 mL of deionized water (for carboxylic acid derivatization) and 5 mL of methylene chloride (for carbonyl derivatization). The carboxylic acid derivatization method by Ford et al. (2007) was modified and used on this deionized water–methylene chloride extract. Briefly, the water–methylene chloride extract was separated by carefully removing the bottom layer (which is the methylene chloride portion of the extract). The carbonyl derivatization method for the methylene chloride filter extract is described above. To the water extract, 1 mL each of 0.8 M aqueous EDC and 0.8 M aqueous TFEA. This solution was vortexed for 1 min then allowed to react for a minimum of 10 min. Then, 5 mL methylene chloride was added and the mixture was vigorously shaken and stored overnight for derivatization reaction completion. The methylene chloride layer was collected into a 7 mL vial, blown to dryness with treated house air, and reconstituted with 100 μL of methanol.

2.3. SPME GC/MS

Sampling to monitor the reaction progress for these terpinolene/O_3/NO_3• product experiments was performed using a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) solid phase micro-extraction (SPME) fiber (Supelco, Milwaukee, WI) assembly which was inserted into a 6.4-mm Swagelok (Solon, OH) fitting attached to a 95 L Teflon®-film bag (the reaction chamber). The reaction chamber contents were sampled for 5 min with the SPME fiber. The SPME was then inserted through a Merlin Microseal (Half Moon Bay, CA) and into the heated injector of the Agilent (Wilmington, DE) 6890 gas chromatograph with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software. The GC settings were the following: injection port was set to 250 °C; and oven temperature began at 40 °C for 2 min and was ramped 10 °C min^{-1}–140 °C and was ramped 20 °C min^{-1}–280 °C and held for 10 min.

For terpinolene/O_3 reaction product yields a 100 μm polydimethylsiloxane (PDMS) fiber was used to sample the Teflon chamber contents. In order to accurately determine terpinolene consumption, its concentration was reduced to approximately 480 ppb (1.2×10^{13} molecule cm^{-3}). The ozone concentration range was between 30 ppb and 100 ppb ($0.75–2.5 \times 10^{12}$ molecule cm^{-3}) of ozone. These concentrations were utilized to avoid analytical system saturation.

2.4. Terpinolene/O_3 and Terpinolene/NO_3• reaction products using PFBHA

Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to stereoisomers of the oximes. 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. In most cases, the *m/z* 181 ion relative intensity for the chromatographic peaks due to terpinolene + O_3 or terpinolene + NO_3• reaction product oximes was the base peak in the mass spectrum and was used to generate selected ion chromatograms. The product data are described below.

The following chronological chromatographic retention time results and mass spectra data were observed utilizing PFBHA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The reaction products' chromatographic peak areas were a function of the initial terpinolene concentration and were observed only after introduction of O_3 or NO_3• to terpinolene/methanol/air mixtures. Derivatization experiments performed in the absence of terpinolene, but in the presence of all other chemicals in the reaction chamber (O_3/NO_3•/air/methanol) did not result in any of the data reported below.

The PFBHA reaction products observed from the terpinolene/O_3 addition to the double bonds are 4-methylcyclohex-3-en-1-one, 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal, methyl glyoxal, 3-oxobutanal, and 6-oxo-3-(propan-2-ylidene)heptanal (listed in Table 1). The PFBHA reaction product observed from the terpinolene/NO_3• via hydrogen abstraction or addition to the double bonds are 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal, methyl glyoxal and 4-oxopentanal (listed in Table 2). Elucidation of the proposed reaction products for terpinolene were facilitated by mass spectrometry of the derivatized reaction product coupled with plausible terpinolene/O_3 or terpinolene/NO_3• reaction mechanisms based on previously published VOC/O_3 or organic compound/NO_3• gas-phase reaction as described below (Spittler et al., 2006; Atkinson and Arey, 2003).

2.5. Terpinolene/O_3 reaction products and yields

2.5.1. Oxime at retention time 17.8 min

The oxime observed with a chromatographic retention time of 17.8 min had ions of *m/z* (relative intensity): 79 (65%), 107 (100%), 181 (45%), 277 (20%), and 306 (34%). In the CI spectra, an M + 1 ion of *m/z* 306 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 4-methylcyclohex-3-en-1-one was based on observed data. The product was also observed in the SPME sampling of the reaction chamber and a yield of approximately 28 ± 6% was determined (Fig. 1).

2.5.2. Oxime at retention time 18.6 min

The oxime observed with a chromatographic retention time of 18.6 min had ions of *m/z* (relative intensity): 43 (48%), 95 (49%), 123 (60%), 181 (100%), 261 (38%), 292 (38%), 306 (50%) and 322 (48%). In the CI spectra, an M + 1 ion of *m/z* 322 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 2-hydroxy-4-methylcyclohex-3-en-1-one was based on observed data.

2.5.3. Oxime at retention time 19.2 and 19 min

The oxime observed with a chromatographic retention time of 19 and 19.3 min had ions of *m/z* (relative intensity): 181 (100%), 265 (35%–10%), 281 (15%–10%), and 448 (40%–7.5%). In the CI spectra, an M + 1 ion of *m/z* 448 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of glyoxal was based on observed data. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment.

2.5.4. Oximes at retention time 19.6 min

The oxime observed with a chromatographic retention time of 19.6 min had ions of *m/z* (relative intensity): 181 (100%), 265 (75%–35%), and 448 (10%–7.5%). In the CI spectra, an M + 1 ion of *m/z* 462 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of methyl glyoxal was based on observed data. The PFBHA-methyl glyoxal oxime was synthesized to confirm this chromatographic assignment.

2.5.5. Oxime at retention time 20.1 min

The oxime observed with a chromatographic retention time of 20.1 min had ions of *m/z* (relative intensity): 181 (100%), 225 (18%–

Table 1
Terpinolene ozone products.

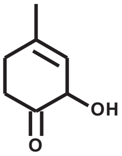
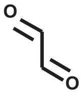
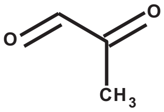
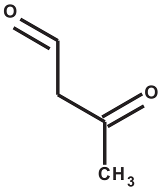
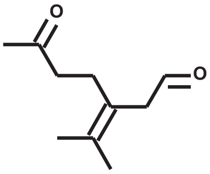
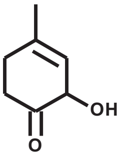
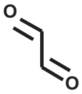
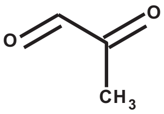
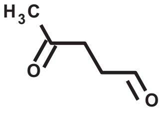
Retention time (min)	Structure	Name	Molecular weight (amu)	CI ions observed
17.8		4-methylcyclohex-3-en-1-one	110	305
18.6		2-hydroxy-4-methylcyclohex-3-en-1-one	126	321
19.2 19.3		Glyoxal	58	448
19.6		Methyl glyoxal	72	462
20.1		3-oxobutanal	86	476
23.5 23.8 24.3 24.4		6-oxo-3-(propan-2-ylidene)heptanal	168	558

Table 2
Terpinolene nitrate radical products hazards.

Retention time (min)	Structure	Name	Molecular weight (amu)	CI ions observed
18.6		2-hydroxy-4-methylcyclohex-3-en-1-one	126	321
19.2 19.3		Glyoxal	58	448
19.6		Methyl glyoxal	72	462
20.5		4-oxopentanal	100	491

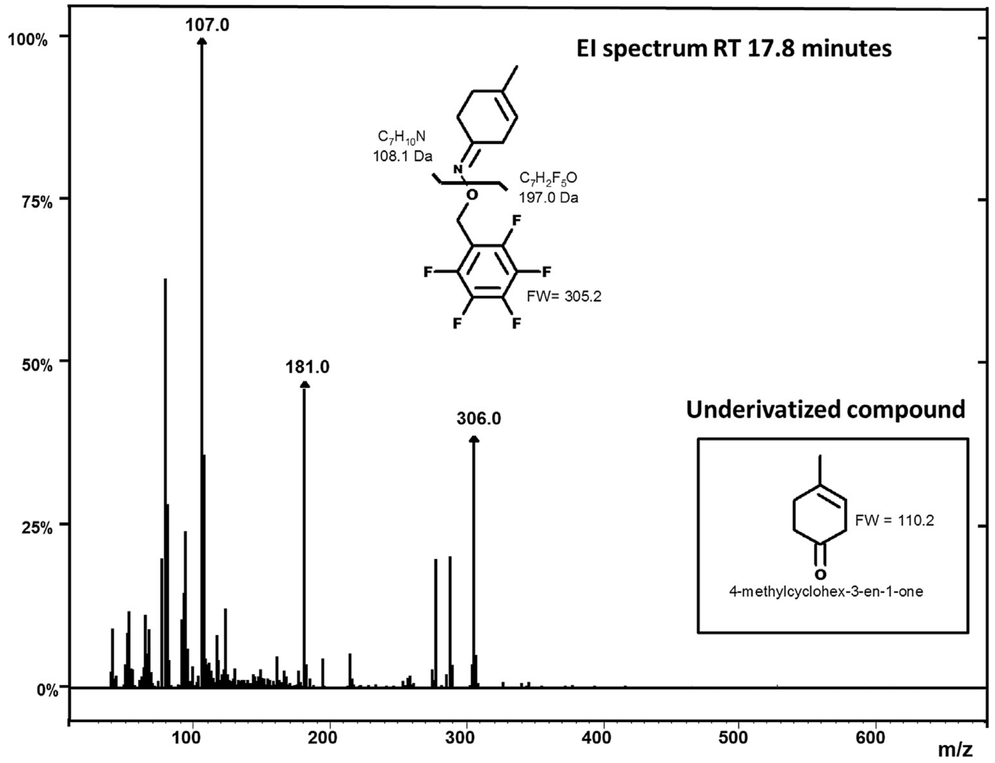


Fig. 1. PFBHA derivative observed in the ozonolysis of terpinolene at retention time of 17.8 min: 4-methylcyclohex-3-en-1-one.

14%) and 476 (20%–17%). In the CI spectra, an M + 1 ion of *m/z* 476 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 3-oxobutanal was based on observed data.

2.5.6. Oxime at retention time 23.5, 23.8, 24.3, and 24.4 min

The oxime observed with a chromatographic retention time of 23.5, 23.8, 24.3, and 24.4 min had ions of *m/z* (relative intensity): 181 (70%–100%) and 361 (75%–100%). In the CI spectra, an M + 1

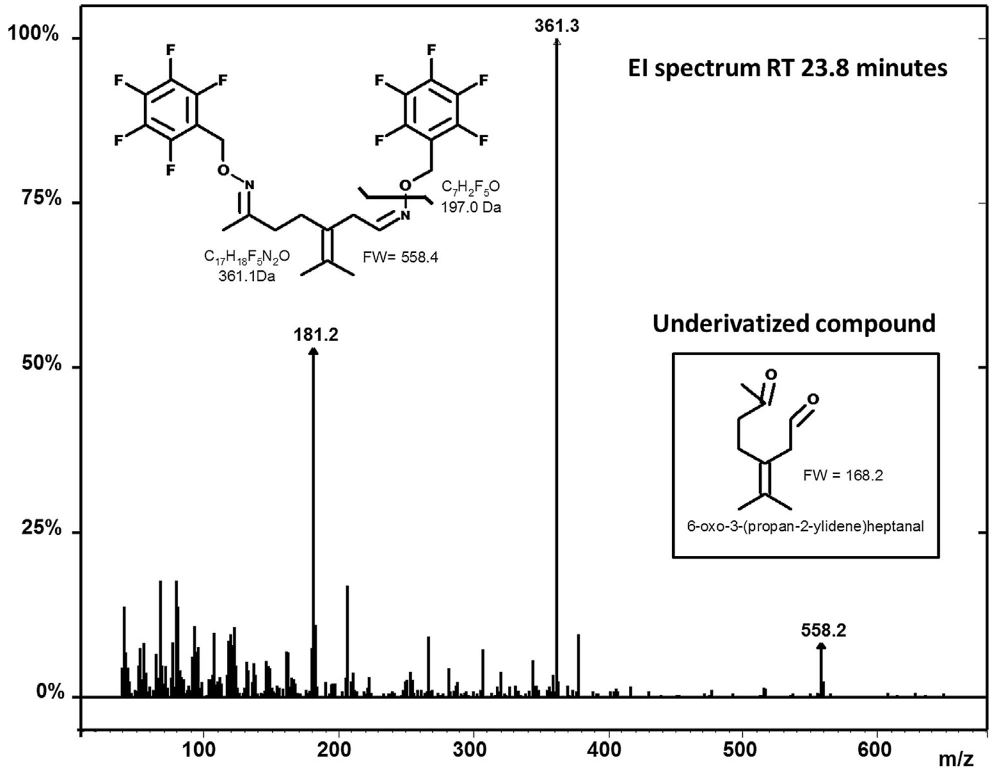


Fig. 2. PFBHA derivative observed in the ozonolysis of terpinolene at retention time of 23.8 min: 6-oxo-3-(propan-2-ylidene)heptanal.

ion of *m/z* 559 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 6-oxo-3-(propan-2-ylidene)heptanal was based on observed data (Fig. 2).

2.6. Terpinolene/NO3• reaction products

2.6.1. Oxime at retention time 18.6 min

The oxime observed with a chromatographic retention time of 18.6 min had ions of *m/z* (relative intensity): 43 (42%), 95 (40%), 123 (58%), 181 (100%), 278 (22%), 306 (350%) and 322 (10%). In the CI spectra, an M + 1 ion of *m/z* 322 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 2-hydroxy-4-methylcyclohex-3-en-1-one was based on observed data.

2.6.2. Oxime at retention time 19.2 and 19.3 min

The oxime observed with a chromatographic retention time of 19.2 and 19.3 min had ions of *m/z* (relative intensity): 181 (100%), 281 (20%–12.5%), and 448 (38%–30%). In the CI spectra, an M + 1 ion of *m/z* 448 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of glyoxal was based on observed data. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment.

2.6.3. Oximes at retention time 19.6 min

The oxime observed with a chromatographic retention time of 19.6 min had ions of *m/z* (relative intensity): 181 (100%), 265 (75%–35%), and 448 (10%–7.5%). In the CI spectra, an M + 1 ion of *m/z* 462 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of methyl glyoxal was based on observed data. The PFBHA-methyl glyoxal oxime was synthesized to confirm this chromatographic assignment.

2.6.4. Oximes at retention time 20.5 min

The oxime observed with a chromatographic retention time of 20 min had ions of *m/z* (relative intensity): 181 (100%), 279 (75%), and 491 (5%). In the CI spectra, an M + 1 ion of *m/z* 491 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 4-oxopentanal was based on observed data. The PFBHA-4-oxopentanal oxime was synthesized to confirm this chromatographic assignment (Fig. 3).

3. Discussion

In the indoor environment, terpenes found in consumer products can transform by reacting with O_3 and NO_3• into oxygenated and nitrated organic species (Aschmann et al., 2002; Muthuramu et al., 1993; Spittler et al., 2006). Importantly exposure to these reaction products may have the potential to cause adverse health effects including asthma and respiratory irritation (Quirce and Barranco, 2010). Terpinolene is a large volume component in many cleaning formulations and its reactivity with O_3 and NO_3• suggests that terpinolene's oxidation will effectively compete with its removal by indoor air exchange (Singer et al., 2006; Ma and Marston, 2009; Hakola et al., 1994; Wilson et al., 1996). While the terpinolene/NO_3• rate constant has been measured (Atkinson and Arey, 2003; Stewart et al., 2013), terpinolene/NO_3• reaction products have not been previously investigated. The terpinolene/O_3 rate constant has been measured (Atkinson and Arey, 2003; Stewart et al., 2013) and the reaction products have been investigated as well (Ma and Marston, 2009; Hakola et al., 1994; Reissell et al., 1999).

3.1. Terpinolene + O_3 reaction products

O_3 can react by adding to the either the exocyclic or endocyclic carbon–carbon double bond of the terpinolene molecule. Using the Environment Protection Agency's AoPWin (EPA, 2000), the calculated ozone addition rate constants to the exocyclic double bond or the endocyclic double bond site are (in units of 10^{-17} cm^3 $molecule^{-1}$ s^{-1}) 120 and 43, respectively. This calculation suggests that O_3 addition to the exocyclic double bond site of terpinolene is favored by almost 3 to

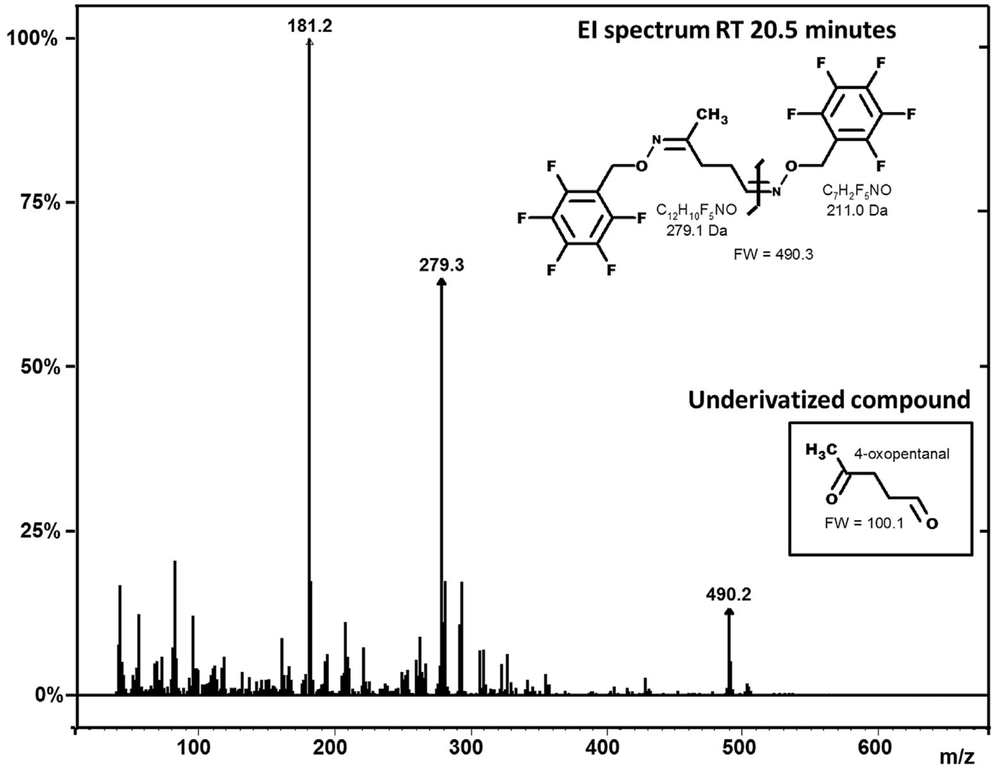


Fig. 3. PFBHA derivative observed in the nitrate radical reaction of terpinolene at retention time of 20.5 min: 4-oxopentanal.

1 to the endocyclic double bond site. Ozone addition to the exocyclic double bond leads to the formation of 4-methylcyclohex-3-en-1-one reported here and previously (Ma and Marston, 2009; Hakola et al., 1994; Reissell et al., 1999) (Fig. 4). Additionally, the 28 ± 6 yield observed in this work and the 50% yield of 4-methylcyclohex-3-en-1-one from the terpinolene + O_3 reaction further supports the reactivity calculation above (Ma and Marston, 2009; Hakola et al., 1994; Reissell et al., 1999). O_3 addition to the endocyclic double bond results in the formation of the observed 6-oxo-3-(propan-2-ylidene)heptanal and is consistent with previous results (Hakola et al., 1994) (Fig. 4). A 1% yield of 6-oxo-3-(propan-2-ylidene)heptanal has been measured previously (Hakola et al., 1994). The reduced terpinolene concentrations used in the yield experiments did not result in an observation of 6-oxo-3-(propan-2-ylidene)heptanal which further supports the preference of exocyclic addition versus endocyclic ozone addition.

Other reaction products observed in terpinolene + O_3 are proposed to be: 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal,

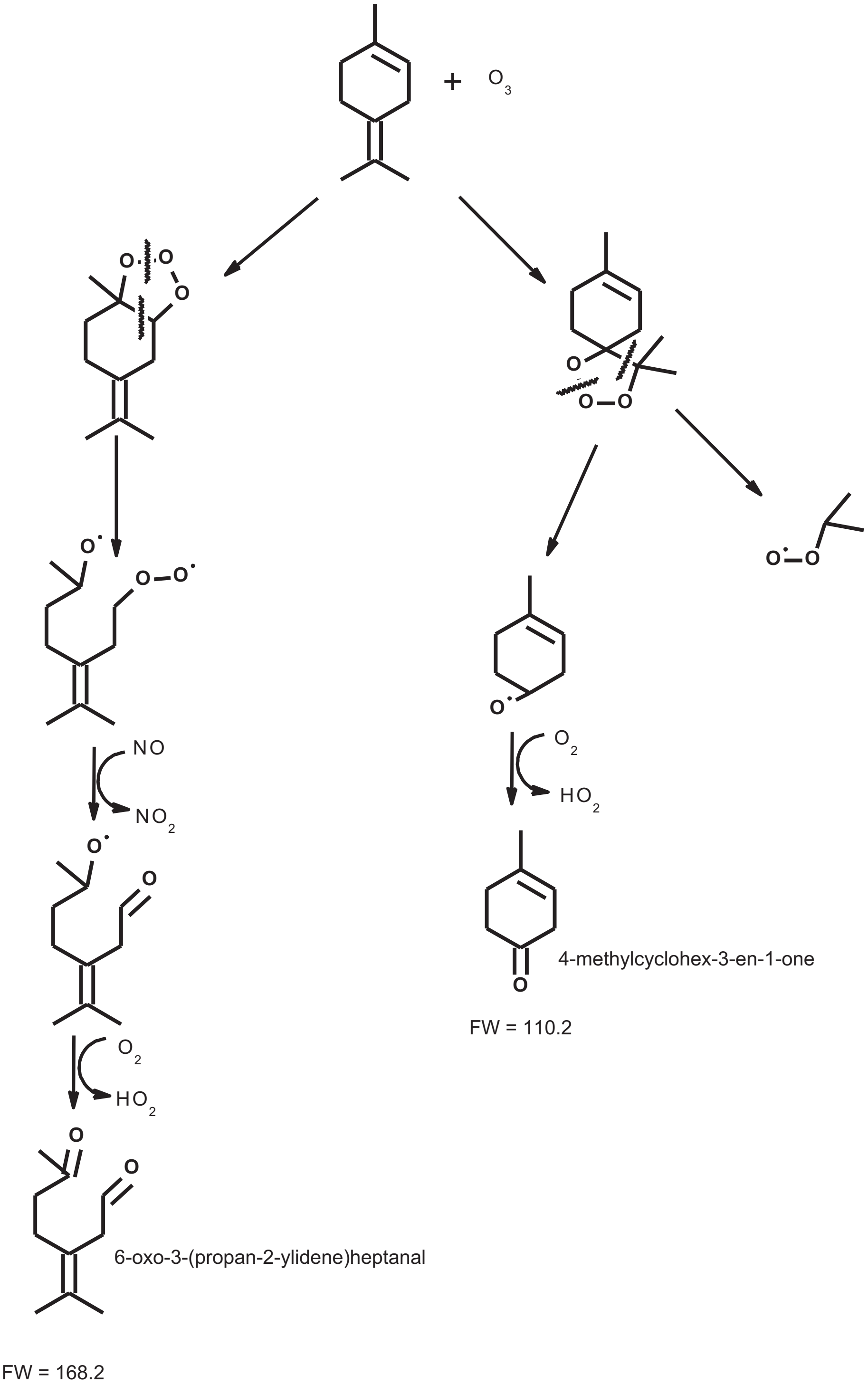


Fig. 4. Terpinolene + O_3 reaction mechanism.

methyl glyoxal and 3-oxobutanal (Table 1). These carbonyl products are unexpected, because they are fragments of the terpinolene molecule and their multi-oxygenated structures suggest they may be secondary reaction products in the experimental system described here. Their formation may possibly be the result of ozone reacting with the double bond of 4-methylcyclohex-3-en-1-one. To explore the likelihood of this possible product formation route, additional rate constant and product yield information is needed. The ozone + 4-methylcyclohex-3-en-1-one rate constant of 7×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Baker et al., 2004) is 27 times smaller than the terpinolene ozone reaction rate constant. The maximum 4-methylcyclohex-3-en-1-one concentration could be 50 ppb (based on a 50% yield and 100 ppb ozone (the limiting reagent)). It is significantly more likely that ozone will react with terpinolene (1 ppm) versus 4-methylcyclohex-3-en-1-one given the experimental conditions. The fragmented products observed could also be the result of OH radicals formed from ozonolysis reacting with 4-methylcyclohex-3-en-1-one. The OH is produced as a byproduct of the reaction forming 4-methylcyclohex-3-en-1-one (Herrmann et al., 2010). The OH + 4-methylcyclohex-3-en-1-one rate constant of 110×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Baker et al., 2004) is 2 times smaller than the terpinolene + OH reaction rate constant. The maximum OH concentration could be 50 ppb (based on a 50% yield and 100 ppb ozone (the limiting reagent)) and it is significantly more likely that OH will react with terpinolene versus the 4-methylcyclohex-3-en-1-one given the experimental conditions. The observed dicarbonyl products are likely the result of O_3 adding to the endocyclic double bond of terpinolene and subsequent fragmentation of that primary ozonide formed. The information suggests that additional molecular rearrangements of the Criegee radical may lead to smaller multi-oxygenated products.

In these experiments, it should be noted that no carboxylic acids were detected in the gas-phase or as particulate. However, Ma and Marston (2009) observed carboxylic acids and tentatively identified five different acids in the gas-phase ozonolysis of terpinolene (2-dicarboxylic acids and 3 carboxylic acids). They determined yields for the carboxylic acids of less than 0.5% (on average). This carboxylic acid yield was observed with 20 ppmv of terpinolene and 15 ppmv of ozone which was 20 and 150 times larger than the experimental conditions used for this work. Under the experimental conditions reported here a 0.5 ppb carboxylic acid concentration would be expected. This is currently below our detection limit (approximately 10's of ppb) and would not be observed using the apparatus described above.

3.2. Terpinolene + NO_3• reaction products

The nitrate radical (NO_3•) can react with terpinolene by H-atom abstraction and/or addition to carbon–carbon double bonds (Spittler et al., 2006). For comparison, the NO_3• reaction with the structurally similar compound limonene leads to the formation of carbonyl compounds and organic nitrates (Spittler et al., 2006). NO_3• addition to terpinolene's carbon–carbon double bonds could yield reaction products similar to the ones previously observed from the terpinolene + O_3 reaction (Hakola et al., 1994; Ma and Marston, 2009; Reissell et al., 1999). The expected product from NO_3• addition to the exocyclic double bonds would be 4-methylcyclohex-3-en-1-one. The expected product for NO_3• addition to the endocyclic double bond would be 6-oxo-3-(propan-2-ylidene)heptanal. Unfortunately, neither 4-methylcyclohex-3-en-1-one nor 6-oxo-3-(propan-2-ylidene)heptanal were detected in NO_3•/terpinolene experiments. To determine if the experimental apparatus or methods were giving erroneous results, back to back O_3/terpinolene and NO_3•/terpinoelene experiments were conducted. 4-methylcyclohex-3-en-1-one and 6-oxo-3-(propan-2-ylidene)heptanal were detected in the terpinolene + O_3 experiments and not in the terpinolene + NO_3• experiments confirming the earlier finding that these two products are not formed in the terpinolene + NO_3• system. The reaction products in terpinolene + NO_3• observed are proposed to be: 2-hydroxy-4-methylcyclohex-3-en-1-one, glyoxal, methyl glyoxal and 4-oxopentanal (See Table 2). These products are formed from the rearrangements and fragmentation of the intermediate species after NO_3• reacts with the double bonds of terpinolene. There also could be products not detected such as organic nitrates, hydroperoxides, PANs, etc. These undetected products could account for the “missing” carbon balance. An organic nitrate detection technique is needed to do a more accurate characterization of the terpinolene/NO_3• reaction products in particular and VOC/NO_3• reaction products in general.

In these terpinolene/NO_3• experiments, it should be noted that no carboxylic acids were detected in the gas-phase or as particulate. The reason carboxylic acids were not detected is explained above.

3.3. Impact to indoor air quality

Indoor environment concentrations of the NO_3• of 2×10^7 molecules cm^{-3} (approximately 1.1 ppt) and O_3 of 1×10^{12} molecules cm^{-3} (approximately 50 ppb) have been previously estimated by Sarwar et al. (2002). Using the rate constants reported by Atkinson and Arey (2003), terpinolene + NO_3•, 97×10^{-12} and terpinolene + O_3, 190×10^{-17} (in units of cm^3 $molecule^{-1}$ s^{-1}) and the above indoor concentrations of NO_3• and O_3, yields pseudo-first order rates (k′) of 8.6 h^{-1} and 8.4 h^{-1}, respectively. Additionally, a lifetime assessment of the primary terpinolene/ozone reaction product can be made using the 4-methylcyclohex-3-en-1-one + NO_3• rate constant, 1.81×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 4-methylcyclohex-3-en-1-one + O_3 rate constant, 6.98×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Baker et al., 2004), yielding the pseudo-first order rates (k’) of 0.3 h^{-1} and 0.1 h^{-1}, respectively. A comparison of these values to a typical indoor air exchange rate of 0.6 h^{-1} (Wilson et al., 1996), suggests that NO_3 radical and O_3 chemistry are an important removal mechanism for terpinolene, but not for 4-methylcyclohex-3-en-1-one. It is apparent that nitrate radical and ozone chemistry could play a critical role in terpinolene's transformation in the indoor environment.

Indoor occupant exposures to terpinolene oxidation products could be ongoing due to repeated application of cleaning products. Oxygenated organic and organic nitrates species have demonstrated the potential to cause a number of adverse health effects including asthma and respiratory irritation (Quirce and Barranco, 2010).

Disclaimer

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