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Surface chemistry of a pine-oil cleaner and other terpene mixtures with ozone on vinyl flooring tiles

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ABSTRACT

Indoor environments are dynamic reactors where consumer products (such as cleaning agents, deodorants, and air fresheners) emit volatile organic compounds (VOCs) that can subsequently interact with indoor oxidants such as ozone (O_3), hydroxyl radicals, and nitrate radicals. Typically, consumer products consist of mixtures of VOCs and semi-VOCs which can react in the gas-phase or on surfaces with these oxidants to generate a variety of oxygenated products. In this study, the reaction of a pine-oil cleaner (POC) with O_3 (100 ppb) on a urethane-coated vinyl flooring tile was investigated at 5% and 50% relative humidity. These results were compared to previous α-terpineol + O_3 reactions on glass and vinyl surfaces. Additionally, other terpene and terpene alcohol mixtures were formulated to understand the emission profiles as seen in the POC data. Results showed that the α-terpineol + O_3 reaction products were the prominent species that were also observed in the POC/O_3 surface experiments. Furthermore, α-terpineol + O_3 reactions generate the largest fraction of oxygenated products even in equal mixtures of other terpene alcohols. This finding suggests that the judicial choice of terpene alcohols for inclusion in product formulations may be useful in reducing oxidation product emissions.

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1. Introduction

The indoor office environment atmosphere is a mixture of hundreds of volatile organic compounds such as alcohols, alkanes, alkenes, terpenes, and phthalates that all react differently with $OH^{\bullet}$, O_3 and $NO_3^{\bullet}$ (Nazaroff and Weschler, 2004). These three reactants have been identified as the key drivers for the complex chemistry that can occur in the indoor environment (Nazaroff and Cass, 1986; Weschler et al., 1992, 1994; Weschler and Shields, 1996; Weschler, 2001; Sarwar et al., 2002; Nojgaard, 2010). Most of the pertinent research has been conducted on individual volatile organic chemicals (VOCs). Therefore, understanding the fate of this complex mixture of indoor office environments has been limited to theoretically combining the chemical research results of individual VOCs.

Recent studies to understand the fate of mixtures in simulated indoor environments have focused on consumer cleaning product formulations. For example, in an effort to understand glycol ether and terpenoid emissions over time for several common cleaning products and air fresheners, chamber experiments were conducted to characterize the emissions from simulated indoor activities (Singer et al., 2006). Five cleaning products either full strength or diluted were applied to surfaces or floors while VOC emissions were collected and analyzed using sorbent tubes and thermal desorption gas chromatography/mass spectrometry. Emissions of limonene, 2-butoxyethanol, dihydromyrcenol, α-terpineol, benzyl acetate and many other VOCs were detected. Limonene for instance had a 0–1 h chamber concentration range after product use of approximately 173–1120 ppb while 2-butoxyethanol's concentration range was 56–477 ppb. 2-Butoxyethanol has an established reference exposure level (REL) by the California Air Resources Board of 2.9 ppm (OEHHA, 1999). This recent work determined realistic chemical composition and concentration for common cleaning products and highlighted possible practices to reduce VOC emissions.

An examination of the primary and secondary products as a result of ozone reacting with a complex VOC mixture has been conducted (Fan et al., 2003). A 23 component VOC mixture, a 21 component VOC mixture (limonene and α-pinene removed from mixture), and a limonene and α-pinene only mixture were all reacted in separate experiments with 40 ppb O_3. Addition of O_3 to the 21 VOC mixture yielded either none or reduced concentrations of the observed products compared to addition of O_3 to the 23 VOC mixture. An additional experiment adding O_3 to the limonene and α-pinene mixture resulted in similar yields of reaction products as observed in the 23 VOC mixture. Observed products included particulate matter, formaldehyde, glyoxal, methyl glyoxal, acetaldehyde, propionaldehyde, and butyraldehyde. This series of experiments are important for demonstrating the influence of

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terpene/ozone chemistry on gas-phase oxygenated organic reaction product concentrations in indoor environments.

The gas-phase reactions of VOCs and semi-VOCs with the indoor oxidant ozone have been studied extensively (Atkinson et al., 1995; Atkinson, 1997; Aschmann et al., 2002, 2003; Ljubic and Sabljic, 2002, 2005; Atkinson and Arey, 2003; Baker et al., 2004); however, equivalent reactions with these compounds on surfaces are limited (Moise and Rudich, 2002; Voges et al., 2007; Ham and Wells, 2008, 2009; Pandrangi and Morrison, 2008; Wells et al., 2008; Gunschera et al., 2009). Several limitations of characterizing surface-O_3 reactions come from (i) accurately collecting emission for reaction product yields, (ii) consistent delivery of O_3 to a surface and (iii) controlling the concentration of a volatile species on a surface in order to determine reaction probabilities. Recently, the O_3 surface-phase reaction of low vapor pressure squalene showed a twenty fold enhancement of reaction rate when compared to the calculated gas-phase reaction (Fruekilde et al., 1998; Wisthaler et al., 2005; Tamas et al., 2006; Coleman et al., 2008; Wells et al., 2008). Voges et al. (2007) also performed surface experiments with the atmospheric terpene, menthenol, on a glass plate with O_3. However, in these experiments, menthenol was oriented so that the OH group was bound to the glass surface by silane-functionalization chemistry. Results showed that the initial reaction probability for ozone interacting with the cyclohexene moiety of the surface-bound terpene increased 5–20 times over the corresponding gas-phase reaction. This observation of higher reaction probabilities indicates improved accessibility of O_3 to the unsaturated carbons of the surface-bound terpene. This result further suggests that if polar groups of VOCs and semi-VOCs in the gas phase reorient themselves as they are adsorbed onto surfaces, then reactions with indoor oxidants can be enhanced.

Several different types of pine-oil based cleaners have been consistently used in hard surface cleaning of flooring and countertops. These cleaners contain a number of terpenoid compounds including: α-terpineol, limonene, terpinolene, and α-pinene. The gas-phase reactions of these compounds (among others not listed) with ozone have been studied (Nunes et al., 2005; Wells, 2005; Jonsson et al., 2006, 2007; Nojgaard et al., 2006; Cain et al., 2007; Sarwar and Corsi, 2007; Vibenholt et al., 2009). Recently, the surface-phase reactions of α-terpineol and dihydromyrcenol (lavender/citrus fragrance) with ozone on glass and vinyl flooring tiles have been investigated (Ham and Wells, 2008, 2009). In both of these experiments, new oxygenated organics were observed compared to gas-phase experiments indicating that the surface can modify the mechanism of formation of reaction products as suggested by Wells et al. (2008) and Voges et al. (2007). The goals of the experiments (described below) are to identify the products from the reaction of O_3 and a pine-oil based cleaner (POC) and other terpene/terpene alcohol mixtures on urethane-coated vinyl flooring tiles and to qualitatively assess these against single component terpene + O_3 surface-phase reactions.

2. Experimental methods

2.1. Materials

(1R)-(+)-α-pinene (98%), α-terpineol (90% Tech grade), (R)-(+)-β-citronellol (98%), dihydromyrcenol (99%), geraniol (⩾99%), limonene (⩾99%), and *O*-(2,3,4,5,6-pentafluoro-benzyl) hydroxylamine hydrochloride (PFBHA) (98+%), were purchased from Sigma Aldrich (St. Louis, MO). A general purpose pine-oil based cleaner packaged as a concentrated liquid was purchased at a local market. Methanol (high-performance liquid chromatography grade) was purchased from Fisher Scientific (Pittsburgh, PA). Water (DI H_2O) was distilled, deionized to a resistivity of 18 MΩ cm and filtered using a Milli-Q® filter system (Billerica, MA). Ultra-high purity nitrogen (UHP N_2) was purchased from Butler Gas (McKees Rocks, PA). Vinyl floor tiles (composition: 80% limestone filler, 12% (vinyl resin – min 60% of binder), 4% plasticizers, 4% stabilizers and processing aids, with urethane finish) that are currently used in the National Institute for Occupational Safety and Health (NIOSH) facility (Morgantown, WV) were purchased from a local building supply center.

2.2. Surface application of prepared mixtures

Two questions have emerged regarding terpene mixture/ozone/surface reactions: (i) do multiple terpene alcohols compete for surface sites and affect gas-phase emissions? and (ii) does the presence of α-terpineol in the mixture dominate emissions due to physical characteristics and chemical structure? To answer these questions, a series of terpene/terpene alcohol + water solutions were formulated (see Table 1): α-terpineol/α-pinene/limonene (TAL), α-terpineol/α-pinene/limonene/dihydromyrcenol (TALD), α-terpineol/geraniol/citronellol/dihydro-myrcenol (TGCD), and α-pinene/limonene/geraniol/dihydromyrcenol (ALGCD). These mixtures were applied to the urethane-coated vinyl flooring surface (as described below) with 100 ppb O_3 in separate experiments and the resulting chromatograms were compared to those in the POC + O_3 experiments.

Mixtures of terpenes/terpene alcohols were prepared according to Table 1. Three μL of each compound were added to 1 mL of deionized water. The POC solution was made according to the directions on the bottle (1/4 cup POC to a gallon of water), but scaled down for 2 mL solutions. All solutions were made in 4 mL amber glass vials and then 0.44 mL (0.44 g on average) was sprayed using a previously described apparatus (Flemmer et al., 2007) on a vinyl floor tile (urethane finish side up) for each of the experiments below. All experiments were conducted at room temperature, 22 ± 2 °C. An aluminum plate (30.5 cm × 30.5 cm × 0.64 cm), with a 14.9 cm diameter hole in the center, was used as a template for spraying the surface. This ensured that the area sampled was directly under the Field and Laboratory Emission Cell (FLEC, Markes International, UK) and that no detectable emissions were collected due to slowly evaporating solvent under the FLEC o-ring.

Before application of any of the described mixtures, the urethane-coated vinyl flooring tiles were aerated to reduce volatile gaseous emissions. New vinyl flooring tiles were placed in a 10 L Teflon chamber filled with UHP N_2 and left overnight. The Teflon chamber was then emptied and allowed to refill and vent using UHP N_2 at 600 mL min^{-1} for approximately 6 h. After 6 h, the chamber was filled again with UHP N_2 and left overnight for experiments the next day. Before beginning an experiment, the chamber was again filled and vented at 600 mL min^{-1} for 45 min. Several background experiments with only air flowing through the FLEC showed no detectable emission products after ventilation, compared to new "non-ventilated" tiles where air only was present (Ham and Wells, 2008). Immediately following the ventilation step, the tile was sprayed and placed under the FLEC.

2.3. FLEC automation and control system (FACS)

The FACS has been described previously (Flemmer et al., 2007). Briefly, the FACS is composed of three stages; the air purification stage, the air humidification stage, and the reactant injection and delivery stage. The air purification stage regulates, cleans, and dries the "in-house" compressed air via two drierite columns and a carbon filter for delivery to the rest of the system. The air humidification stage mixes both dry and humid air to create and deliver the desired humidity for the duration of the experiment. The reactant ejection and delivery stage introduces the reactant, at the desired

Table 1
Chemical components of mixtures that were formulated then applied to vinyl flooring tiles in surface-O_3 experiments.

Chemical	Mixture 1 (TAL)	Mixture 2 (TALD)	Mixture 3 (TGCD)	Mixture 4 (ALGCD)
α-terpineol	X	X	X	
α-pinene	X	X		X
Limonene	X	X		X
Dihydromyrcenol		X	X	X
Geraniol			X	X
Citronello			X	X

X indicates that 3.0 μL of “pure” chemical was injected to 1 mL of DI H_2O in a 4 mL amber vial.

concentration, into the air stream and delivers the air to the FLEC for the experiment.

2.4. Mixture solutions + O_3 on a vinyl tile at 50% or 5% RH (FACS)

For all mixtures (Table 1) and the POC solution, the FACS was initialized using the following parameters: the reactant concentration (i.e., O_3) was set to 100 ppb, the relative humidity was set to 50% or 5% (depending on experiment), and the flow rate through FLEC was set to 300 mL min^{-1}. High concentration ozone (45–50 ppm) was prepared in advance by placing a UV lamp (Jelight ozone generator, Model 600, Irvine, CA) in a 70 L Teflon chamber filled with clean dry air. The ozone/air mix was then regulated to 100 ppb for the air flow through the FLEC.

2.5. Vinyl tile – Rinse experiments

A series of rinse experiments were conducted by placing a vinyl flooring tile (coated/uncoated with POC or Mixture solutions) under the FLEC and then exposing with O_3 (100 ppb in air) or air for 12 h at 5% or 50% RH. After exposure the vinyl tiles were rinsed with 6 mL of HPLC grade methanol into a custom Pyrex container (Ham and Wells, 2008, 2009). The rinsate was then collected and split into two vials. The first vial contained 2.0 mL of sample, while the second vial contained the sample remaining in the Pyrex container. To the first vial, 200 μL of PFBHA (20 mM in ACN) was added then left overnight to complete carbonyl derivatization. PFBHA derivatizes products with carbonyl substructures to facilitate detection by gas chromatography/mass spectrometry (Yu et al., 1998).

2.6. Sample collection and analysis

Emissions from POC or Mixture reactions (FACS) were collected in a 100 mL glass impinger immersed in a thermostated water bath at 0 ± 0.5 °C controlled by an immersion chiller (EK45, Fisher Scientific, Pittsburgh, PA) and connected to the output of the FLEC using 0.64 cm O.D. Teflon tubing. To the impinger, 14.7 mL of HPLC grade methanol was added. Output air from the FLEC at 300 mL min^{-1} was bubbled through the impinger for 12 h.

At the end of the 12 h sampling period, the solution left in the impinger (~4 mL) was divided into two 4 mL amber vials. The first vial (labeled 1A) was filled with 2.0 mL of solution from impinger. The remaining solution (~1.5–2 mL) was placed in the second vial (vial 1B). To identify reaction products (i.e., aldehydes, ketones, and dicarbonyls), 200 μL of PFBHA (20 mM in ACN) was added to the 1A vials. These vials were then left overnight to allow for the reaction to go to completion. No PFBHA was added to the 1B vials.

After reaction completion, the 1A vials were blown to complete dryness using UHP N_2 then reconstituted in 100 μL of methanol. The 1B vials were unaltered and injected as pure samples. This was done to monitor the concentration of POC or mixture solutions over time.

All samples were then analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.25 mm I.D., 30-m long, 1 μm film thickness) column and the following GC oven parameters: 60 °C for 1 min, then 20 °C min^{-1} to 170 °C, then 3 °C min^{-1} to 280 °C and held for 5 min. One μL of each sample (Vial 1A or 1B) was injected

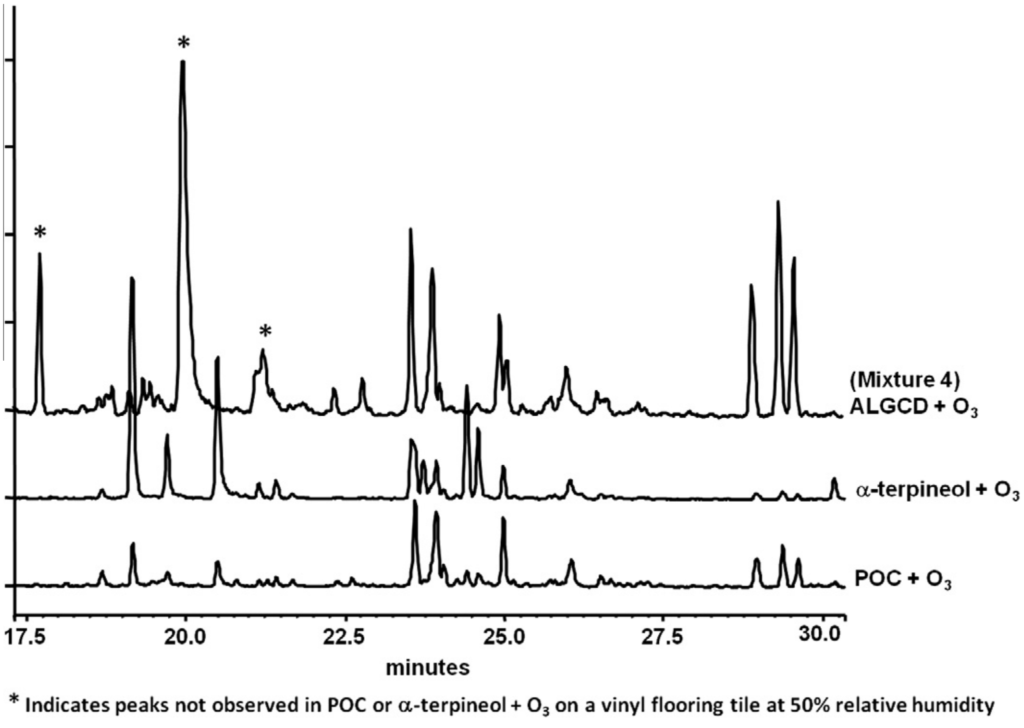
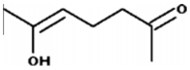
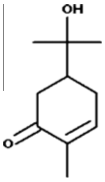
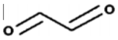
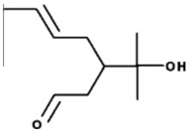
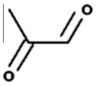
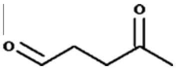


Fig. 1. Chromatograms obtained from POC + O_3, α-terpineol + O_3, and ALGCD mixture + O_3 reactions on vinyl flooring tiles.

Table 2
Reaction products observed due to α-terpineol and POC reactions with O_3 at RH = 50% on vinyl flooring tiles.

Retention time (min)	Name * indicates proposed identity	Molecular weight	Structure	CI ions (observed)
19.2	6-hydroxyhept-5-en-2-one	128		324
20.5	5-(l-hydroxy-l-methylethyl)-2-methylcyclohex-2-en-l-one	168		364
23.6 23.9	Ethanedial (glyoxal)	58		449
24.4 24.6	(5E)-3-(2-hydroxypropan-2-yl)hept-5-enal	170		364
25.0	2-oxopropanal (methylglyoxal)	72		463
28.9 29.4 29.6	4-oxopentanal	100		491

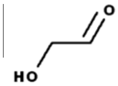
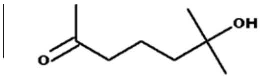
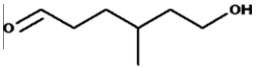
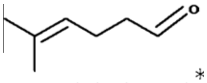
in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 60 °C for 1 min then 180 °C min^{-1} to 250 °C and held to the end of the chromatographic run. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from *m*/*z* 40–650. Each sample was analyzed in duplicate. Acetonitrile was the chemical ionization 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.

3. Results and discussion

Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes, Fig. 1. 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' (generic structure: $F_5C_6CH_2ON = C(R_1)(R_2)$) mass spectra included an ion at *m*/*z* 181 ($[CH_2C_6F_5]^+$ fragment) with a large relative intensity (>40%) and a $[\text{PFBHA oxime} + 181]^+$ 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_3 reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms (Yu et al., 1998).

Common POCs consist of a mixture of a number of terpenoid compounds in differing concentrations. Although the formulations can vary widely, the three major terpenes found in POCs are α-terpineol, terpinolene, and d-limonene as observed in GC/MS analysis and reported in recent literature (Singer et al., 2006). When appropriately diluted in water (per instructions) and 0.4 g of this solution is applied to a vinyl flooring surface (as described above) in the presence of 100 pbb of ozone, a number of carbonyl com-

Table 3
Additional reaction products that were observed but were not due to α-terpineol reactions with O_3 at RH = 50% on vinyl flooring tiles.

Retention time (min)	Structure * indicates proposed identity	POC mixture	Mixture 1 (TAL)	Mixture 2 (TALD)	Mixture 3 (TGCD)	Mixture 4 (ALGCD)
9.9	 glycolaldehyde	–	–	–	X	X
17.2 17.7	 6-hydroxy-6-methyl-2-heptanone	–	–	X	X	X
19.9	 6-hydroxy-4-methylhexanal	–	–	–	X	X
21.1	 5-methyl-4-hexenal *	–	–	–	X	X

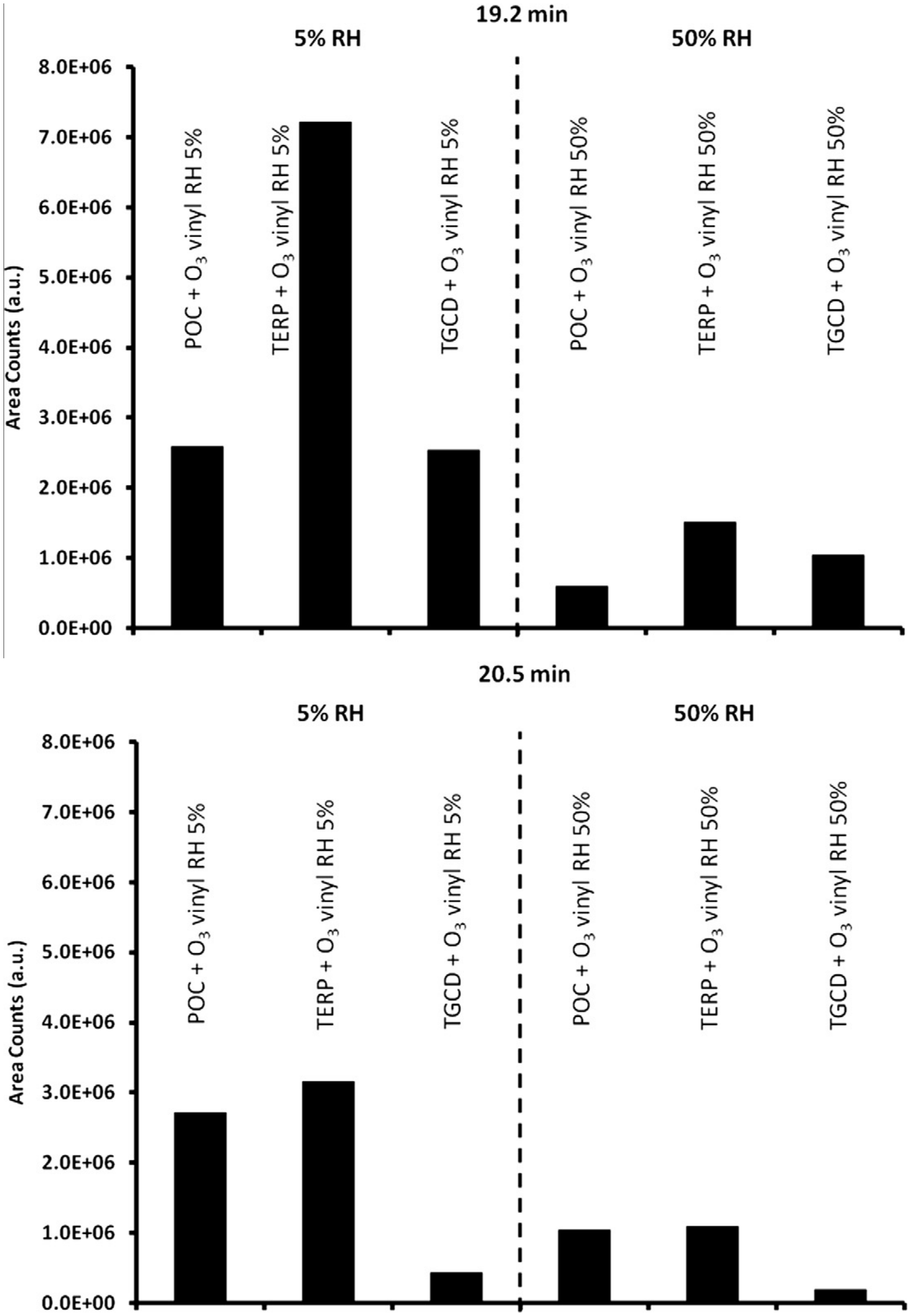


Fig. 2. Averaged peak areas for POC + O_3, α-terpineol + O_3, and TGCD mixture + O_3 reactions at 5% and 50% relative humidity for the (a) 19.2 and (b) 20.5 min peaks proposed identities for these retention times are shown Table 2.

pounds were subsequently emitted into the gas-phase as shown in Fig. 1. When O_3 was absent from the air flowing to the surface, no carbonyl oxidation products were observed.

Recently the surface-phase reactions of α-terpineol with O_3 on both glass and vinyl flooring tiles were investigated (Ham and Wells, 2008). Results showed the formation of a number of carbonyl species that emulated those observed in the POC + O_3 experiments seen here. When chromatograms from α-terpineol + O_3 and POC + O_3 were overlayed and the resulting mass spectra were analyzed, the observed peaks from POC + O_3 matched three of the six products (at retention times: 19.2, 20.5, and 24.4 & 24.6 min, Table 2) observed in α-terpineol/O_3 experiments indicating that the α-terpineol reaction products dominate the POC + O_3 gas-phase emission profile. The other products that were observed (glyoxal, methylglyoxal, and 4-oxopentanal) are likely formed through multiple reaction pathways with other terpenes, including α-terpineol, as previously observed in both the gas-phase and surface-phase reactions (Wells, 2005; Ham et al., 2006; Forester et al., 2007a,b; Ham and Wells, 2008, 2009).

In the TALD + O_3 and TGCD + O_3 experiments, a number of oxidation products (retention times 9.9, 17.2 & 17.9, 19.9, 21.1, Table 3) were generated that were not due to reactions of O_3 with α-terpineol. Both the 9.9 min peak (glycolaldehyde) and 21.1 min peak (5-methyl-4-hexenal) are likely products from geraniol, based on mechanisms in the literature and previous geraniol + O_3 gas-phase studies (Nunes et al., 2005; Forester et al., 2007b). The peaks observed at 17.2 and 17.9 min (6-hydroxy-6-methyl-2-heptanone) are due to the dihydromyrcenol + O_3 reaction as previously observed in surface-phase reactions on both glass and vinyl flooring tiles (Ham and Wells, 2009). The peak observed at 19.9 min (6-hydroxy-4-methylhexanal) is an oxidation product that was also observed in previous citronellol/O_3 gas-phase studies (Ham et al., 2006).

Previous studies of terpene alcohol reactions on surfaces have indicated that the OH moiety of these species orients itself to the surface resulting in a change in the rate and reaction pathways (Voges et al., 2007; Ham and Wells, 2008, 2009). In these series of experiments surface coverage from the solution mixtures was calculated to be on the order of 4–12 terpenoid molecules thick. It is possible that these terpenoid layers above the first OH bound layer exist in a terpenoid rich solution as "islands" or "pools" where O_3 may penetrate to initiate reactions. If the OH bound layer is responsible for the observed products, it is anticipated that increasing the number of terpene alcohols (TAL < TALD < TGCD) in a mixture applied to a surface and initiating a reaction with ozone will result in a possible reduction in some reaction product emission profiles, i.e., peak areas, due to surface site competition. When these mixtures were applied to the surface, those peaks attributable to α-terpineol/O_3 reactions did not change in peak area. This indicates that α-terpineol may have a more favorable attachment to the surface compared to the other terpene alcohols.

This observation could be explained by investigating some physical characteristics of the terpenoid compounds in mixtures as they are applied to the surface. This analysis could potentially be used to predict the reactive chemistry of other mixtures. Recently, the octanol–air partition coefficients (K_{OA}) were calculated for several semivolatile organic compounds (SVOCs) to characterize chemical migration or redistribution in indoor environments (Weschler and Nazaroff, 2008). Those results showed that log K_{OA}'s greater than 10 are indicative of strongly absorbing species that could persist for hundreds to thousands of hours in indoor environments (Meylan and Howard, 2005; Weschler and Nazaroff, 2008). Viewing the vinyl surface as simply another environmental surface, the calculated log K_{OA}'s for α-terpineol, dihydromyrcenol geraniol, citronellol, α-pinene and limonene are 6.6, 6.3, 6.8, 6.5, 3.6, and 4.3, respectively (EPA, 2000). Additionally, the Henry's law constants (HLC) for α-terpineol, dihydromyrcenol, geraniol, citronellol, α-pinene and limonene were calculated: 1.6×10^{-5}, 4.1×10^{-5}, 5.9×10^{-5}, 5.7×10^{-5}, 1.1×10^{-1}, 3.8×10^{-1} atm-m^3 mol^{-1}, respectively (EPA, 2000). While the calculated log K_{OA}'s for the terpene alcohols are similar, the HLCs for these terpenoids indicated that α-terpineol's lower value suggests that its emission will be slower thus enhancing its reaction probability with ozone. Furthermore, the lower log K_{OA} values and higher HLCs for limonene and α-pinene coincide with no observation of carbonyl oxidation products from limonene/O_3 or α-pinene/O_3 reactions on the surface. These calculations are consistent with the observed reaction product emission data. When α-terpineol was removed from the mixture (ALGCD/O_3 experiment), no peaks were observed at retention times of 19.2, 20.5, and 24.4 or 24.6 min indicating that those products are specific to α-terpineol + O_3. Additionally, peaks associated with geraniol, citronellol, and dihydromyrcenol did not change in peak area compared to TGCD + O_3 experiments indicating the competition for surface sites at this particular concentration of terpenoid compounds does not affect gas-phase emissions.

All data described in the previous paragraphs were collected at 50% relative humidity to simulate a typical indoor environment. However, humidity can have a significant effect on the formation/observation of reaction products as compounds partition between the gas and aerosol phases (Jonsson et al., 2006; Vesna et al., 2009; Warren et al., 2009). To investigate the influence of relative humidity on product emissions, POC + O_3, α-terpineol + O_3, and TGCD + O_3 experiments were conducted using urethane-coated vinyl flooring tiles and 5% relative humidity. Additionally, contrasting the emission profiles from the simplest (one component), four-component and an actual consumer product mixture was done to provide more insight into the impact multiple components, as well as humidity, have on surface ozone reactions. In these experiments, an increase in reaction product peak area was observed for all oxidation products listed in Table 2 from POC/O_3, α-terpineol + O_3, and TGCD + O_3 experiments. Fig. 2a and b show the increase in peak areas for both the 19.2 (6-hydroxyhept-5-en-2-one) and 20.5 (5-(1-hydroxy-1-methyl ethyl)-2-methylcyclohex-2-en-1-one) minute products at 5% compared to 50% relative humidity. The increase in peak area suggests that at the lower humidity reaction products partition more into the gas-phase as water is less available to form aggregate clusters. It could also mean that these terpene alcohols compete for surface sites with water which will affect the surface concentration (density) of carbon–carbon double bonds available for reaction with ozone. Furthermore, at lower humidity it is possible that the sprayed terpenoid solution evaporates faster resulting in more α-terpineol molecules reacting at the air-surface interface. However, when the surface rinsate was analyzed no difference in reaction product peak area was observed between 5% and 50% relative humidity, suggesting that relative humidity does not significantly impact terpene alcohol surface attachment.

4. Conclusions

The results from these experiments demonstrated that the presence of α-terpineol in a POC or other simulated mixture can be a predictor of the emissions from terpene/ozone surface reactions. This can be clearly seen in Fig. 1 where POC + O_3, α-terpineol + O_3 and ALGCD + O_3 are compared. The presence of terpene alcohols on surfaces may be the main source of carbonyl reaction product emissions in indoor environments. This information could be used to predict consumer product emissions and gives insight into more accurate indoor occupant exposure assessments.

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.

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