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Surface chemistry reactions of α-terpineol [(R)-2-(4-methyl-3-cyclohexenyl)isopropanol] with ozone and air on a glass and a vinyl tile

Abstract The surface-phase reaction products of α-terpineol [(R)-2-(4-methyl-3-cyclohexenyl)isopropanol] with ozone (O_3), air or nitrogen (N_2) on both a glass and vinyl flooring tile were investigated using the recently published FLEC Automation and Control System (FACS). The FACS was used to deliver O_3 (100 ppb), air or N_2 to the surface at a specified flow rate (300 ml/min) and relative humidity (50%) after application of a 1.6% α-terpineol solution in methanol. Oxidation products were detected using the derivatization agents: *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine and *N,O*-bis(trimethysilyl)trifluoroacetamide. The positively identified reaction products were glyoxal, methylglyoxal and 4-oxopentanal. The proposed oxidation products based on previously published VOC/O_3 reaction mechanisms were: 4-methylcyclohex-3-en-1-one, 6-hydroxyhept-en-2-one, 3-(1-hydroxy-1-methylethyl)-6-methylcyclohex-2-en-1-one) and one surface-enhanced reaction product: 5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-en-1-one. Though similar products were observed in gas-phase α-terpineol/O_3 reactions, the ratio of the reaction products were different suggesting stabilization of larger molecular weight species by the surface. Emission profiles of these oxidation products over 72 h are also reported.

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Key words: α-Terpineol; Ozone; Reaction products; Surface chemistry.

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Practical Implications
Volatile organic compounds (VOCs) can interact with indoor initiators [such as hydroxyl radicals (OH•), ozone and nitrate radicals (NO_3•)] to form a number of oxygenated by-products in the gas-phase. However, when VOCs are applied to or are present on the surface, heterogeneous chemistry with indoor initiators can also occur. The surface can influence the reaction mechanism to produce new surface reaction products. The work, described here, shows the interaction of α-terpineol (major component of pine oil) with ozone and air on both glass and vinyl flooring. These results demonstrated emissions of oxygenated organic compounds as a result of reaction and that further investigations of this chemistry are required to accurately estimate indoor occupant exposures.

Introduction

Surfaces can play an important role in the reactive chemistry of the indoor environment. They can remove gas-phase chemical species through adsorption, emit chemicals because of material contents or through chemical coatings (i.e. cleaning or decorative finishes) and catalyze chemical reactions. Importantly, surfaces can have a bearing on all these parameters at the same time. Unlike indoor environment gas-phase chemistry, indoor surface chemistry is not limited by air exchange rates; reactants can be continually in contact with one another and kinetic and/or concentration limitations can be overcome (Colombo et al., 1993; Deng and Kim, 2004; Grøntoft, 2002, 2004; Grøntoft et al., 2004). Additionally, surfaces may have the potential to enhance reaction rates that otherwise would occur very slowly in the gas-phase. The many variations of indoor surfaces' chemical compositions and physical forms make defining and understanding their impact on the indoor environment complicated yet important (Klenø et al., 2001; Meininghaus and Uhde, 2002; Won et al., 2001).

Ozone (O_3) is influential in the indoor environment as both a reactant and an initiator species for formation of the hydroxyl (OH•) and nitrate (NO_3•) radicals (Nazaroff and Cass, 1986; Sarwar et al., 2002; Weschler, 2000, 2001; Weschler and Shields, 1996).

There have been many investigations of gas-phase reactions between O_3 and volatile organic compounds (VOC) found in the indoor environment (Jonsson et al., 2006; Pommer et al., 2004; Wells, 2005). There have also been several investigations of the interaction between O_3 and surfaces. For example, Kleno et al. observed the uptake of O_3 on a number of indoor surface materials. One surface of interest was nylon carpet which seemed to have an unlimited capacity to adsorb O_3 (Klenø et al., 2001). Furthermore, Morrison et al. determined that carpet exposed to a mean indoor concentration of 2.7 ppb O_3 could result in long-term (years) emissions of aldehyde and ketone species (Morrison and Nazaroff, 2000, 2002a,b). Recent investigations of the heterogeneous chemistry of ventilation systems when coupled with O_3 surface adsorption/surface emission results continue to demonstrate the dynamic chemistry of the indoor environment (Fick et al., 2004). From this study, it can be seen that indoor surfaces can serve as reaction sites and thus influence the indoor environment, but describing the reaction mechanism(s) and kinetics has been challenging.

Pseudo-first order gas-phase rate constants for reactions between O_3 and VOCs relevant to the indoor environment have been measured or calculated (Nazaroff and Weschler, 2004). Typically, many of these reactions are slower than typical building air exchange. However, as stated above, indoor surface chemistry reactions are not constrained by air exchange (Morrison and Nazaroff, 2002b). As a consequence, it is not yet possible to estimate rates, yields or air concentrations of reactants and products that participate in surface reactions, based purely on available kinetics and mechanisms of the corresponding gas-phase reactions. Nevertheless, recent studies of secondary organic aerosols have highlighted effects of surface on the reaction rate (Kahan et al., 2006; Kwamena et al., 2004, 2006; Moise and Rudich, 2000, 2001, 2002; Moise et al., 2002). For example, the surface-phase reactions of O_3 with polycyclic aromatic hydrocarbons (PAHs) attached to sea salt or organic substrates have been shown to have different reaction rates compared with PAH/O_3 gas-phase reactions (Kwamena et al., 2004, 2006; Moise and Rudich, 2000; Thornton and Abbatt, 2005). This research has also shown the formation of oxygenated organic compounds such as aldehydes and ketones on aerosol surfaces.

Because the surface has been shown to influence VOC chemistry, it is expected that the reaction products that are formed could be different and potentially impact indoor occupant exposures. Occupant exposure as a result of indoor chemistry is an important input towards assessing the health effects of the indoor environment. For example, recent work by Anderson et al. (2007) using the local lymph node assay and QSAR modeling demonstrated both glyoxal and methylglyoxal as sensitizers. The presence of a surface can either enhance the formation/emission of these oxygenated organic products or lead to the formation of distinct surface-mediated products. Investigations of the surface/VOC/O_3 chemistry are important for more complete assessments of occupant exposure.

Surface cleaning is a very common activity which can introduce many VOCs or semi-VOCs into the indoor environment. One compound of recent interest is α-terpineol, a significant component of pine oil cleaners. While α-terpineol emission has been observed from surfaces treated with cleaners, this compound can also remain on the surface to be available for reaction with O_3 (Destaillats et al., 2006; Nazaroff and Weschler, 2004; Singer et al., 2006a). The goals of the experiments (described below) are to identify oxidation products from the reaction of O_3 and α-terpineol on both glass and vinyl surfaces and qualitatively assess the emission pattern and compare against those for gas-phase reactions. These experiments have taken advantage of a recently developed reactant delivery system: the Field and Laboratory Emission Cell (FLEC®) Automation and Control System (FACS) (Flemmer et al., 2007). The FACS automatically controls humidity, O_3 concentration and airflow over a surface for an extended period of time. This device has been used to initiate both surface chemistry and collect surface emissions to more accurately describe the influence surfaces have on the indoor environment.

Experimental methods

Materials

α-Terpineol (90% Tech grade), *O*-(2,3,4,5,6-pentafluorbenzyl)hydroxylamine hydrochloride (PFBHA) (98 + %), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (99 + %) and acetonitrile (ACN) (≥99.93%) were purchased from Sigma Aldrich (St Louis, MO, USA). Methanol (high-performance liquid chromatography grade) and methylene chloride (Optima) was purchased from Fisher Scientific (Pittsburgh, PA, USA). Ultra-high purity nitrogen (UHP N_2) was purchased from Butler Gas (McKees Rocks, PA, USA). Heat-resistant borosilicate glass plates (25.4 × 25.4 × 0.32 cm) were purchased from McMaster-Carr (Atlanta, GA, USA). 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, USA) were purchased from a local building supply center.

Surface application of α-terpineol

α-Terpineol solutions (20 μl in 1 ml of methanol) were made in 4 ml amber glass vials and then the entire solution was sprayed using a previously described apparatus (Flemmer et al., 2007) on either a glass plate or a vinyl floor tile (urethane finish side up) for each of the experiments below. A (30.5 × 30.5 × 0.64 cm) aluminum plate, with a 17.8-cm diameter hole in the center, was used as a template for spraying the surface (i.e. glass or vinyl). This insured that the area sampled was directly under the FLEC and that no detectable emissions were collected because of slowly evaporating solvent under the FLEC o-ring.

Before application of the α-terpineol solution, the vinyl tiles were aerated to reduce gaseous emissions. New vinyl 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 for approximately 6 h. After 6 h, the chamber was pressurized 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 for 45 min. Several background experiments with only air flowing through the FLEC showed no emission products after ventilation, compared with new 'non-ventilated' tiles where air only was present. Similar experiments with a 'clean' glass tile also showed no emission products. Immediately following the ventilation step, the tile was sprayed and placed under the FLEC.

FLEC automation and control system

The FACS has been described previously (Flemmer et al., 2007). A brief description is given here. 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 NIOSH facility 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 injection and delivery stage introduces the reactant, at the desired concentration, into the air stream and delivers the air to the FLEC for the experiment. Figure 1 illustrates how air or O_3 is introduced to the surface that has been coated with a chemical of interest (i.e. α-terpineol).

The entire system is controlled by a standard desktop computer which houses an analog output card, a multifunction data acquisition card and a multi-port serial card. The control program is a C/C++ Windows application that was written in-house and utilizes libraries provided by National Instruments (Austin, TX, USA).

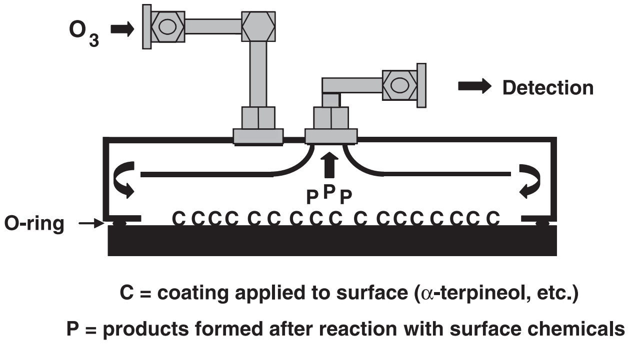


Fig. 1 Illustration of ozone deposition through FLEC, production emission and detection

α-Terpineol + air or N_2 on vinyl or glass tile (FACS)

For the α-terpineol/air experiment, the FACS was initialized using the following parameters: the reactant concentration (i.e. O_3) was set to zero, the relative humidity was set to 50% and the flow rate through FLEC was set to 300 ml/min. During N_2 only experiments, a UHP N_2 tank was connected to FACS inlet.

α-Terpineol + O_3 on vinyl or glass tile (FACS)

In this experiment, the FACS was initialized using similar parameters as above, except for the reactant concentration (O_3) which was set to 100 ppb. High concentration O_3 (45–50 ppm) was prepared in advance by placing a UV lamp (Jelight ozone generator, Model 600, Irvine, CA, USA) in a 70-l Teflon chamber filled with clean dry air. The O_3/air mix was then regulated to 100 ppb for the airflow through the FLEC.

α-Terpineol + O_3 on glass or vinyl tile for 12 h, then switch to air for remaining (FACS)

In this experiment, the FACS was initialized using the same parameters as above. A glass or vinyl tile was sprayed with the α-terpineol solution described above, then placed under the FLEC. After 12 h, the O_3 concentration was set to zero and clean, dry air was allowed to flow through the system for the remaining 72 h of sampling.

O_3 only on vinyl tile (FACS)

A 'ventilated' tile was placed under the FLEC with the same parameters above: $[O_3] = 100$ ppb, relative humidity = 50% and FLEC flow rate = 300 ml/min. Samples were then collected over 72 h.

α-Terpineol + O_3 in an impinger

An α-terpineol solution with 5 μl of 90% Tech grade α-terpineol was mixed with 14.7 ml of methanol and placed in the 50 ml glass impinger used for all FACS experiments. With the FLEC removed, O_3 (100 ppb) was flowed through the FACS to the impinger for 12 h at a flow rate = 300 ml/min and relative humidity = 50%. After 12 h, the sample was collected derivatized and analyzed, as described below.

α-Terpineol + O_3 in a Teflon chamber

Experiments were conducted to determine if any of the products seen from the surface would be observed in the gas-phase. α-Terpineol (300–470 ppb) was injected into a Teflon bag (approximately 85 l) reaction chamber with filtered house air at 5 or 50% relative humidity. To initiate the reaction, O_3 (approximately 100 ppb) was injected using a gas-tight syringe into the reaction chamber. These concentrations were based on previous indoor environment research (Singer et al., 2006b; Wainman et al., 2000; Weschler, 2000). Two experimental reaction set samples were collected approximately 20 min after O_3 injection. One reaction set sample consisted of a reaction chamber sample without O_3 and a reaction chamber sample after O_3 addition. The other reaction sample set was the same as above except cyclohexane (approximately 266 ppm) was added to the reaction mixture to scavenge OH production. Approximately 20 l samples of the chamber contents were collected at ~3–4 l/min through an impinger filled with 3 ml methanol. Then 200 μl of a 20-mM PFBHA solution was added to the remaining methanol sample from the impinger. These samples were blown to dryness using UHP N_2 and then reconstituted with 100 μl methanol and analyzed as described below. All FACS and bag experiments (described above) were at least done in duplicate.

Glass or vinyl tile – rinse experiments

A series of rinse experiments were done by placing a glass or vinyl tile (coated/uncoated with α-terpineol) under the FLEC and then exposing with O_3 (100 ppb) or air for 72 h. These experiments were carried out with no attempt to collect emissions with the impinger. The following experiments were performed at relative humidity = 50% and a FLEC flow rate of 300 ml/min (See Table 1): α-terpineol/glass/air, α-terpineol/glass/O_3, uncoated/vinyl/O_3, α-terpineol/vinyl/O_3, α-terpineol/vinyl/air. In a separate experiment, a 'ventilated' tile was rinsed with methanol only. A rinse of a vinyl tile that had been sprayed with the α-terpineol solution after 5 min was also done to observe the maximum concentration.

After exposure, glass or vinyl tiles were rinsed with 6 ml of HPLC grade methanol into a custom pyrex container. The container is a 30.5 cm diameter × 30.5 cm high × 0.64 cm thick cylinder with a gradual slope that begins approximately 10.2 cm from the top lip. The slope ends with a 5-cm diameter hole which extends another 8.9 cm before closing. The tiles were placed in the cylinder and rinsed. The rinsate was then collected and split into two vials. The first vial contained 1.5 ml of sample, whereas the second vial contained the remaining sample left in the pyrex container. To the first vial, 200 μl of PFBHA (20 mM in ACN) was added then left overnight for reaction completion.

Table 1 List of rinse experiments

	Surface	Chemical	Reactant	Notes
1	Glass	α-Terpineol	Air	Tile rinsed after 72 h under FLEC
2	Glass	α-Terpineol	O_3, 100 ppb	Tile rinsed after 72 h under FLEC
3	Vinyl	–	–	'Ventilated' tile, was not placed under FLEC
4	Vinyl	–	O_3, 100 ppb	Tile rinsed after 72 h under FLEC
5	Vinyl	α-Terpineol	–	α-Terpineol solution was sprayed, waited 5 min and then tile was rinsed
6	Vinyl	α-Terpineol	O_3, 100 ppb	Tile was rinsed after 72 h under FLEC
7	Vinyl	α-Terpineol	Air	Tile rinsed after 72 h under FLEC

Sample collection and analysis

Emissions from α-terpineol reactions (FACS) were collected in a 50 ml glass impinger (p/n 652650-2440; Kontes, Vineland, NJ, USA) immersed in an ice-water bath at 0°C and connected to the output of the FLEC using 0.64 cm O.D. Teflon tubing. Collection efficiency experiments using this impinger system at 0 and 25°C were conducted with α-terpineol. Results showed that α-terpineol was collected 30% more efficiently at 0°C. To the impinger, 14.7 ml of HPLC grade methanol was added. Output air from the FLEC at 300 ml/min was bubbled through the impinger for 12 h. At the end of the 12 h, another impinger base filled with 14.7 ml of methanol was quickly inserted so as to minimize the interruption to flow in the system. This process was repeated until 72 h of total sampling was obtained for a total of six samples.

At the end of each 12 h sampling, the solution left in the impinger (~4 ml) was divided into two 4 ml amber vials. The first vial (vials 1A–6A) was filled with 2.0 ml of solution from impinger. The remaining solution (~1.5–2 ml) was placed in the second vial (vials 1B–6B). To identify reaction products (i.e. aldehydes, ketones and dicarbonyls), 200 μl of PFBHA (20 mM in ACN) was added to vials 1A–6A. These vials were then left overnight to allow for the reaction to go to completion. PFBHA derivatizes products with carbonyl substructures to facilitate detection by gas chromatography/mass spectrometry (GC/MS) (Yu et al., 1998). No PFBHA was added to vials 1B–6B.

After all samples were collected, vials 1A–6A were blown to complete dryness using UHP N_2 then reconstituted in 100 μl of methanol. Vials 1B–6B were unaltered and injected as pure samples. This was carried out to monitor the concentration of α-terpineol over time.

For further identification of alcohol products, derivatization with BSTFA was employed. 100 μl aliquots were removed from vials 1B–6B and put in 2 ml vials with 100 μl glass inserts for direct injection. The remaining solution in vials 1B–6B were treated with 200 μl of PFBHA and allowed to react overnight. These vials were then blown to dryness using UHP N_2. Vials were then reconstituted with 100 μl of hexane:methylene chloride (1:1) with subsequent addition of 20 μl of commercially available BSTFA. These PFBHA/BSTFA solutions were heated to approximately 60°C for 45 min to complete the silylation and then 1 μl of the solution was injected into the Varian 3800/Saturn 2000 GC/MS system (Yu et al., 1998).

All samples were then analyzed using a Varian (Palo Alto, CA, USA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by a J&W Scientific (Folsom, CA, USA) 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 to 170°C, then 3°C/min to 280°C and held for 5 min. One microliter of each sample was injected 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 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 to 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.

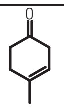
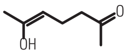
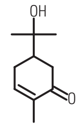
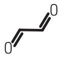
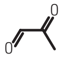
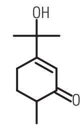
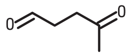
Results

Observed reaction products

Derivatization of non-symmetric carbonyls using PFBHA or PFBHA/BSTFA typically resulted in multiple chromatographic peaks because of geometric isomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple because 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 [PFBHA oxime + 181]$^+$ ion (as a result of reactions in the ion trap mass spectrometer). In most cases, the m/z 181 ion relative intensity for the chromatographic peaks because of α-terpineol + 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. The mass spectra of compounds that were additionally derivatized with BSTFA contained m/z 73 ions from the $[Si(CH_3)_3]^+$ fragments (Yu et al., 1998). The product data for both FACS and rinse experiments are described below (See Table 2). A summary table comparing the products observed from both FACS and rinse experiments are shown in Table 3a,b. To address possible oxidation reactions occurring in the impinger, experiments were conducted with α-terpineol added directly to the impinger and exposed to O_3 for 12 h which resulted in the observation of all the reported reaction products. However, the detection of these reaction products in 24–72 h surface chemistry experiments cannot be explained by oxidation reactions occurring in the impinger. As the measured α-terpineol concentration in the impinger during surface-phase experiments decreases to < 10% of its maximum after 12 h and a fresh impinger solution is inserted every 12 h, it is evident that the α-terpineol concentration collected in the impinger is not sufficient to explain the results of the surface chemistry experiments.

Emission profiles (described below for each product retention time, see Figures 2–4) were determined by

Table 2 List of products observed from the α-terpineol + air/ozone on glass/vinyl tile

Retention time (min)	Name	Molecular weight (amu)	Structure	CI ions observed
16.4	4-methylcyclohex-3-en-1-one[a]	110		306
19.6	6-hydroxyhept-5-en-2-one[a]	128		324
20.9 21.6 21.9	5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-en-1-one	168		364
24.4	Ethanedial (glyoxal)[a]	58		449
25.5	2-oxopropanal[a] (methylglyoxal)	72		463
26.6	3-(1-hydroxy-1-methylethyl)-6-methylcyclohex-2-en-1-one	168		364
29.7 30.1 30.4	4-oxopentanal[a]	100		491

[a]Observed in gas-phase reactions Wells (2005).

Table 3 Comparison of products observed in α-terpineol + air/ozone on glass/vinyl tile. (a) Products observed in FACS experiments. (b) Products observed in rinse experiments

	Chromatographic retention time of products (mm)					
	16.4	19.6	20.9, 21.6, 21.9	Glyoxal	Methylglyoxal	26.6
(a) FACS experiments						
α-Terpineol/glass/air	−	+	−	−	−	+
α-Terpineol/vinyl/air	−	+	−	−	−	+
α-Terpineol/glass/O_3	+	+	+	+	+	+
α-Terpineol/vinyl/O_3	+	+	+	+	+	+
Vinyl/O_3	−	−	−	−	−	−
α-Terpineol/vinyl/O_3 + cyclohexane	−	+	+	+	+	+
α-Terpineol/Teflon bag/O_3	−	+	−	+	+	+
(b) Rinse experiments						
α-Terpineol/glass/air	−	+	+	+	+	+
α-Terpineol/vinyl/air	−	−	−	−	−	+
α-Terpineol/vinyl (0 h)	−	−	−	−	−	+
α-Terpineol/glass/O_3	−	−	+	+	+	+
α-Terpineol/vinyl/O_3	−	+	−	−	−	+
Vinyl/O_3	−	−	−	−	−	−
'Ventilated' vinyl tile	−	−	−	−	−	−

+, product was observed; −, product was not observed.

integrating the peak area of the emission product at each of the 12 h sampling times.

α-Terpineol at retention time 8.4 min

Vials 1B–6B (no PFBHA added) showed only one peak at a retention time of 8.4 min. This peak identified as α-terpineol had ions of m/z (relative intensity): 136 (100%), 121 (40–45%), 95 (15–25%) and 81 (50–70%).

α-Terpineol was observed in all FACS experiments from vials 1B–2B where α-terpineol was sprayed onto either a glass or vinyl surface. Rinse experiments after 72 h only showed α-terpineol in the following experiments: α-terpineol/vinyl/wait 5 min and rinse, α-terpineol/vinyl/O_3, α-terpineol/vinyl/air.

The emission profile of α-terpineol over a 72-h sampling period for its reaction with O_3, air or N_2 on a vinyl tile shows large emission within the first 12 h and sharp decrease to < 10% in the next 12 h on all surfaces. The emission profile of α-terpineol + O_3 on vinyl does show a greater decrease in α-terpineol concentration over time vs. the same reaction with air or N_2. This suggests that the reaction with O_3 is faster than its removal by air or N_2 alone.

Oxime at retention time 16.4 min

The oxime observed with a chromatographic retention time of 16.4 min had ions of *m*/*z* (relative intensity): 79 (70–75%), 107 (70–75%), 181 (100%), 195 (10–15%), 277 (10–20%) and 306 (5–10%). Using acetonitrile for chemical ionization, an M + 1 ion of *m*/*z* 306 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of

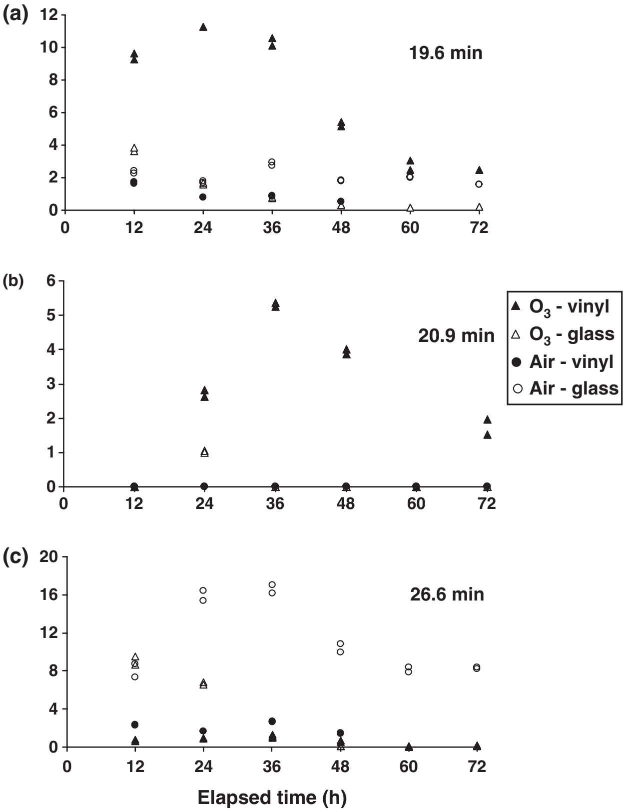


Fig. 2 Emission profile of α-terpineol + ozone or air products on a vinyl or glass tiles (FACS experiments): (a) oxime at 19.6 min, (b) oxime at 20.9 min, (c) oxime at 26.6 min

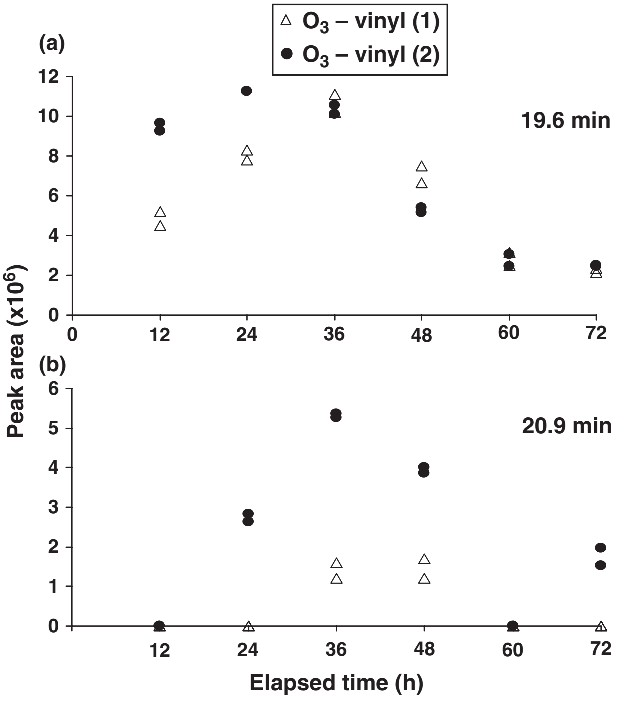


Fig. 3 Comparison of emission profiles for two separate data sets for α-terpineol + ozone on vinyl flooring tile: (a) oxime at 19.6 min, (b) oxime at 20.9 min

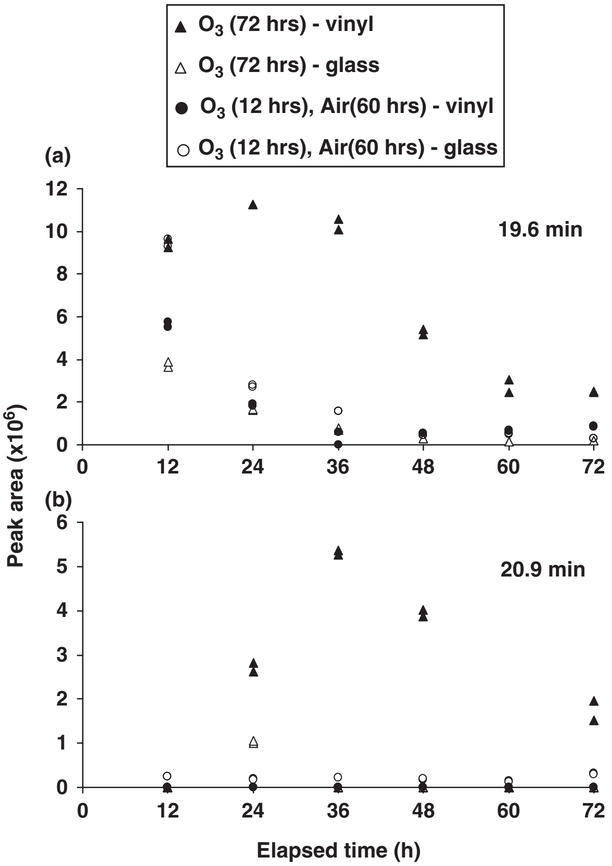


Fig. 4 Comparison of emission profiles of α-terpineol + ozone (72 h) or ozone (12 h), then air (60 h) on glass and vinyl. (a) oxime at 19.6 min, (b) oxime at 20.9 min

4-methylcyclohex-3-en-1-one was based on observed data (Wells, 2005).

The oxime at 16.4 min was only observed in the 1A vials in the following FACS experiments: α-terpineol/glass/O_3 and α-terpineol/vinyl/O_3. This products' emission profile exhibited an emission maximum at 12 h and rapid decrease to <30% at 12–24 h sampling. This product was not observed in any of the rinse experiments.

Oxime 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): 107 (40–50%), 126 (40–45%), 181(75–85%), 288 (75%), 305 (100%) and 324 (25–35%). Using acetonitrile for chemical ionization, an M + 1 ion of *m*/*z* 324 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 6-hydroxy-hept-5-en-2-one was based on observed data.

PFBHA/BSTFA derivatization of the oxime at 19.6 showed a chromatographic peak shift in retention time to 22.4 min. Using acetonitrile for chemical ionization, an M + 1 ion of *m*/*z* 396 was observed. BSTFA adds *m*/*z* 72 to the PFBHA-derivatized oxime, indicating the presence of an OH group. This data were used to further verify the proposed assignment of the 19.6 min peak (Wells, 2005).

This product was observed in the following FACS experiments (Table 3a): α-terpineol/glass/air, α-terpineol/glass/O_3, α-terpineol/vinyl/O_3 and the α-terpineol/O_3/bag experiments. The 19.6-min oxime was also observed in the α-terpineol/N_2/vinyl experiment, but was less than 7% of the peak observed in α-terpineol/O_3/vinyl. In the rinse experiments (Table 3b), this product was only seen in the α-terpineol/glass/air and α-terpineol/vinyl/O_3.

Figure 2a displays the emission profiles of the oxime observed at 19.6 min over a 72-h sampling period for the reactions of α-terpineol with O_3 on a vinyl tile and a glass tile, and α-terpineol + air on a vinyl tile and glass tile. For α-terpineol + O_3 on a vinyl tile, the emission profile showed an increase of the product at 12 h, and an emission maximum that occurs between 12 and 24 h of sampling and subsequent decay. For both the α-terpineol + O_3 reaction on a glass tile and α-terpineol + air on vinyl, the emission profile had an emission maximum at 0–12 h and decay to zero during the next 24 h. Interestingly, α-terpineol + air on glass, displayed a steady emission of this product over 72 h.

Comparison of emission profiles for duplicate data sets for the 19.6 oxime is shown in Figure 3a. These duplicate sets, which were performed approximately 3 months apart, show that the emission profile trends are approximately the same. These results suggest that the method of sample collection and analysis were consistent.

In both of the α-terpineol + O_3 on glass tile and the α-terpineol + O_3 on vinyl for 12 h, then switch to air experiment (Figure 4a), the emission profile for the 19.6 min oxime exhibited an emission maximum at 12 h and steady decrease to <10% of the original concentration during the 60–72 h samples.

Oxime at retention time 20.9, 21.6 and 21.9 min

The chromatographic peaks for the oxime observed at 20.9, 21.6 and 21.9 min had ions of *m*/*z* (relative intensity): 97 (30–35%), 110 (50–60%), 166 (100%), 181 (90%), 195 (10–15%), 288 (5–15%), 305 (5%) and 364 (5–15%), see Figure 5a. Using acetonitrile for chemical ionization, an M + 1 ion of *m*/*z* 364 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-en-1-one was based on observed data.

PFBHA/BSTFA derivatization of the oximes at 20.9, 21.6 and 21.9 min showed a chromatographic peak shift in retention time to 22.4 min. These peaks co-eluted with the PFBHA/BSTFA peak observed for the 19.6 min oxime. Using acetonitrile for chemical

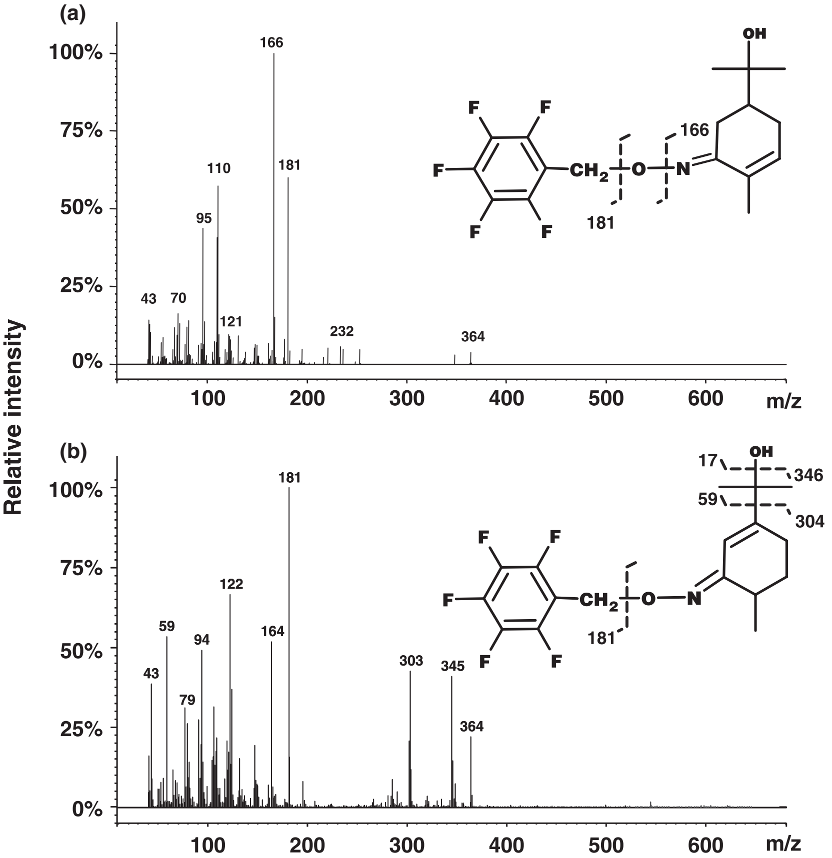


Fig. 5 EI mass spectra of PFBHA oximes at (a) 20.9 min, (b) 26.6 min

ionization, an M + 1 ion of *m/z* 436 was observed. This data were used to further verify the proposed assignment of the 20.9, 21.6 and 21.9 min peaks.

The oxime at 20.9, 21.6 and 21.9 min was observed in the following FACS experiments (Table 3a): α-terpineol/glass/O_3, α-terpineol/vinyl/O_3. This product was observed in the α-terpineol/O_3/bag experiments at both 5 and 50% relative humidity; however, the relative peak areas compared with other products that were observed were much smaller than that observed in surface chemistry experiments. This oxime was observed in the α-terpineol/glass/air and α-terpineol/glass/O_3 rinse experiments only (Table 3b).

Figure 2b displays the emission profiles of the oxime observed at 20.9 min for the reactions of α-terpineol with O_3 on a vinyl and glass tile, and α-terpineol + air on a vinyl and glass tile. The oxime at observed at 21.6 and 21.9 min exhibited the same emission profiles as the 20.9 min peak. For α-terpineol + O_3 on a vinyl flooring tile, the emission profile showed an emission maximum that occurs between 24 and 36 h of sampling and subsequent decay. For the α-terpineol + O_3 reaction on a glass tile, the emission profile had an emission maximum at 12–24 h of sampling; however, the emission maximum was approximately 10% of that seen in α-terpineol + O_3 on vinyl. α-terpineol + air on vinyl and glass showed no formation/emission of this product.

A comparison of emission profiles for duplicate data sets for the 20.9 min oxime is shown in Figure 3b. These duplicate sets, which were performed approximately 3 months apart, show a similar emission profile trend with the carbonyl compound emitting in the 24–36 h sample.

In the α-terpineol + O_3 on glass tile for 12 h, then switch to air experiment, the emission profile (Figure 4b) for the 20.9, 21.6 and 21.9 min oxime showed no formation/emission of this product over 72 h of sampling on glass or vinyl flooring tile.

Glyoxal [ethanedial, HC(=O)C(=O)H]

The oxime observed with a chromatographic retention time of 24.6 min had ions of *m/z* (relative intensity): 195 (5–15%), 163(30–40%), 181 (100%) and 448 (5–15%). The *m/z* 448 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 58. Using acetonitrile for chemical ionization, an M + 1 ion of *m/z* 449 was observed for the PFBHA-derivatized sample. The PFBHA–glyoxal oxime was synthesized to confirm this chromatographic assignment (Wells, 2005; Yu et al., 1998).

Glyoxal was observed in the following FACS experiments: α-terpineol/glass/O_3, α-terpineol/vinyl/O_3. This product was also seen in the α-terpineol/O_3/bag experiment. In the rinse experiments, glyoxal was only observed in α-terpineol/glass/air and α-terpineol/glass/O_3.

No emission profile was determined for glyoxal because the concentration decreased below the detection limit after 24 h.

In the α-terpineol + O_3 on glass tile for 12 h, then switch to air experiment, the emission profile for glyoxal displayed a maximum at 0–12 h sampling and sudden decrease to zero in the 12–72 h samples.

Methylglyoxal [2-oxopropanal, $CH_3C(=O)C(=O)H$]

The oxime observed with a chromatographic retention time of 25.9 min had ions of *m/z* (relative intensity): 195 (5–15%), 147(20–25%), 181 (100%), 265 (20–25%) and 462 (5–10%). The *m/z* 462 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 72. Using acetonitrile for chemical ionization, an M + 1 ion of *m/z* 463 was observed for the PFBHA-derivatized sample. The PFBHA–methylglyoxal oxime was synthesized to confirm this chromatographic assignment (Wells, 2005; Yu et al., 1998).

Methylglyoxal was observed in the following FACS experiments: α-terpineol/glass/O_3, α-terpineol/vinyl/O_3. This product was also seen in the α-terpineol/O_3/bag experiment. In the rinse experiments, methylglyoxal was only observed in α-terpineol/glass/air and α-terpineol/glass/O_3.

For α-terpineol + O_3 on a glass tile, the emission profile had an emission maximum that occurs between 0 and 12 h of sampling and subsequent decay. For the α-terpineol + O_3 reaction on a vinyl flooring tile, the emission profile showed a steady release of this oxime over the 0–36 h of sampling and then slow decay to ~15% of its maximum after 72 h. α-Terpineol + air on both glass and vinyl showed emission of methylglyoxal over 72 h; however, these profiles were not determined because of low signal.

Similar to the emission profile for glyoxal, in the α-terpineol + O_3 on glass tile for 12 h then switch to air experiment, the emission profile for methylglyoxal showed a maximum at 0–12 h sampling and sudden decrease to zero in the 12–72 h samples. In the vinyl experiments, methylglyoxal exhibited the same trend as on glass.

Oxime at retention time 26.6 min

The oxime observed with a chromatographic retention time of 26.6 min had ions of *m/z* (relative intensity): 95 (50–60%), 122 (70–80%), 147 (40–50%), 181 (100%), 302 (40–45%), 345 (30–35%) and 364 (10–15%), see Figure 5b. Using acetonitrile for chemical ionization, an M + 1 ion of *m/z* 364 was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 3-(1-hydroxy-1-methylethyl)-6-methylcyclohex-2-en-1-one was based on observed data.

PFBHA/BSTFA derivatization of the oxime at 26.6 showed a chromatographic peak shift in retention time to 28.3 min. Using acetonitrile for chemical ionization, an M + 1 ion of *m/z* 436 was observed. This data were used to further verify the proposed assignment of the 26.6 min peak.

The oxime at 26.6 min was observed in all FACS and rinse experiments in which α-terpineol was applied to either a glass or vinyl surface. This product was observed in the α-terpineol/O_3/bag experiment, but was less than 10%, by peak area, as seen in the surface chemistry experiments.

Figure 2c displays the emission profiles of the oxime observed at 26.6 min over a 72-h sampling period for the reactions of α-terpineol with O_3 on a vinyl tile and glass tile, and α-terpineol + air on a vinyl and glass tile. For α-terpineol + O_3 on a glass tile, the emission profile had an emission maximum that occurs between 0 and 12 h of sampling and subsequent decay. For the α-terpineol + O_3 reaction on a vinyl flooring tile, the emission profile showed a steady release of this oxime over the 72 h of sampling. α-Terpineol + air on vinyl exhibited the same trend and approximate concentrations as observed in the α-terpineol + O_3 on vinyl. Interestingly, the α-terpineol + air on glass displayed an increase in concentration between 12 and 24 h of sampling, an emission maximum at 24–36 h, and slow decrease to ~50% of the emission maximum in the 60–72 h sample.

In the α-terpineol + O_3 on glass tile for 12 h, then switch to air experiment, the emission profile for the 26.6 min oxime showed an emission max at 0–12 h, a slow decrease to ~20% of emission max at 24–36 h, and then plateaued and steadily emitted for the 36–72 h samples. Vinyl tile experiments exhibited a steady emission (approximately 10% of that observed on glass) over 72 h.

4-Oxopentanal [4OPA, $CH_3C(=O)(CH_2)_2C(=O)H$]

The oximes observed at 29.7, 30.1 and 30.4 min had ions of *m/z* (relative intensity): 181 (100%), 207 (25–50%), 279 (60–75%), 490 (5%). The *m/z* 490 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 100. Using acetonitrile for chemical ionization, an M + 1 ion of *m/z* 491 was observed for the PFBHA-derivatized sample. The PFBHA–4OPA oxime was synthesized to confirm this chromatographic assignment (Wells, 2005; Yu et al., 1998). 4OPA was not observed in any of the rinse experiments. No emission profiles were determined as this product was not emitted after 12 h.

Discussion

The gas-phase kinetics and reaction products of α-terpineol with the hydroxyl radical (OH•) and O_3 has been recently studied (Wells, 2005). Based on reaction product formation, O_3 was shown to react as expected with the carbon–carbon double bond of α-terpineol with a measured rate constant of (3.0 ± 0.2) × 10^{-16} cm^3/molecule·s. The significant products, based on chromatographic peak areas, reported from the α-terpineol/O_3 gas-phase reactions were: 6-hydroxyhept-5-en-2-one and methylglyoxal.

To determine the possibility of gas-phase reactions contributing to the observance of products in the surface chemistry experiments, the reaction rate based on experimental parameters was calculated for α-terpineol + O_3. Based on the reaction rate constant determined previously of $k_{\alpha\text{-terpineol} + O_3}$ = (3.0 ± 0.2) × 10^{-16} cm^3/molecule·s and an [O_3] = 100 ppb, a pseudo-first order reaction rate of 2.66 h^{-1} can be calculated. Given an air exchange rate of 514 h^{-1} in the FLEC based on (internal FLEC volume = 35 ml and flow rate = 300 ml/min), it is expected that the gas-phase reaction is much too slow to compete with air exchange. Therefore, oxidation products that were observed are primarily generated through surface chemistry reactions.

Oxime at retention time 16.4 min (4-methylcyclohex-3-en-1-one)

This product was observed in previous α-terpineol/OH• gas-phase measurements and as an α-terpineol/O_3 surface reaction product. A likely mechanism for the formation of this product involves the subsequent formation of OH• as a result of the α-terpineol/O_3 reaction (Kroll et al., 2001, 2002).

Oxime at retention time 19.6 min (6-hydroxyhept-5-en-2-one)

This oxime has also been observed in previous α-terpineol/O_3 gas-phase measurements and was observed as an α-terpineol/O_3 surface reaction product. The proposed mechanism for formation of this product is shown in Figure 6. O_3 can add to the carbon–carbon bond forming the ozonide, structure (**I**). Cleavage between the oxygen–oxygen bond of the ozonide and subsequent cleavage of the carbon–carbon along with the addition of O_2 leads to structure (**III**). The peroxyradical in structure (**III**) can abstract hydrogen from the adjacent carbon which leads to formation of a new carbon-carbon double bond, seen in structure (**VI**). This energy rich intermediate can react further with O_2 with subsequent losses of OH• and a $-CH_3$ group to form 6-hydroxyhept-5-en-2-one. As a result of this reaction, glyoxal is another possible product from this intermediate, structure (**VI**). Glyoxal was observed in small yields which supports the proposed mechanism for formation.

6-hydroxyhept-5-en-2-one was also observed in the α-terpineol + air on glass and vinyl experiments where no O_3 was present. The presence of this product may be due to an impurity with the standard sample; however, the observance of emission over 72 h indicates that this product is formed as a result of reaction. In the absence of O_3, there seems to be another radical driven mechanism that results in ring opening of α-terpineol.

As with most of the reaction products that were observed, the 19.6 min oxime has a greater affinity for the vinyl surface over that of the glass as indicated by rinse experiments (Table 3b). This is evident in Figure 2a where emission goes approximately to zero after 72 h on glass, whereas the emission on vinyl continues to emit for a longer period of time. The 19.6 min oxime emission decreases to less than 10% in ~60 h after the O_3 was stopped, see Figure 4a.

Oxime at retention times 20.9, 21.6 and 21.9 min [5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-en-1-one]

This product was observed in the α-terpineol/O_3/Teflon bag gas-phase measurements and was also observed as an α-terpineol/O_3 surface reaction product. The proposed mechanism for its formation is shown in Figure 6. Again, O_3 can add to the carbon–carbon double bond forming the ozonide, structure (**I**). If cleavage occurs on the opposite side of the oxygen–oxygen bond as in the 19.6 min oxime, the energy rich intermediate, structure (**II**), may form. The peroxyradical can then abstract the adjacent hydrogen on the carbon ring with subsequent loss of HO_2, structure (**V**). The carbon ring can then be stabilized by the formation of a new carbon–carbon double bond. The oxygen radical that remains is then stabilized by the formation of the carbonyl.

The emission profile of the 20.9, 21.6 and 21.9 min oxime suggests that this is a reaction product as indicated by the emission maximum occurring after 36 h, see Figure 2b. Unlike the 19.6 min oxime, a greater affinity for the glass surface over vinyl was observed (Table 3b). Additionally, as in the O_3 switch to air experiments for the 19.6 min oxime, the 20.9, 21.6 and 21.9 min oxime emission decreases to less than 10% in ~60 h after the O_3 was stopped, see Figure 4b.

Glyoxal (ethanedial)

This product was observed in previous α-terpineol/O_3 gas-phase measurements, and was also observed as an α-terpineol/O_3 surface reaction product. The proposed

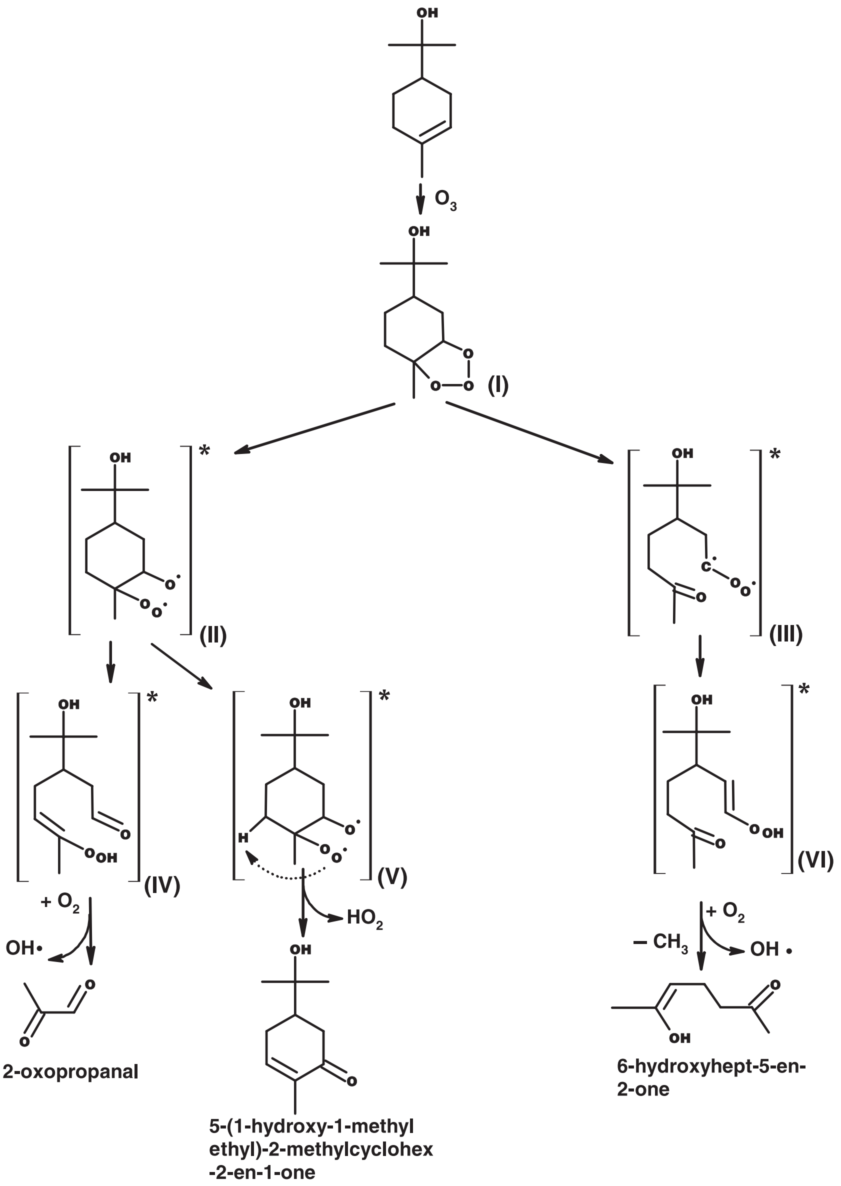


Fig. 6 Proposed mechanism for formation of α-terpineol/O_3 surface reaction products

mechanism for glyoxal is discussed in detail in the discussion section for 6-hydroxyhept-5-en-2-one.

Methylglyoxal (2-oxopropanal)

This product was observed in previous α-terpineol/O_3 gas-phase measurements and was also observed as an α-terpineol/O_3 surface reaction product. The proposed mechanism for the formation of methylglyoxal is shown in Figure 6. O_3 adds to the carbon–carbon double bond forming the ozonide, structure (**I**). As with 20.9, 21.6 and 21.9 min oxime, if cleavage occurs on the opposite side of the oxygen–oxygen bond as in the 19.6 min oxime, the energy rich intermediate, structure (**II**), may form. The peroxyradical can then abstract the adjacent hydrogen on the carbon ring. To stabilize the carbon radical that was formed, the ring can open up and form a new carbon–carbon double bond. Subsequent OH• loss and addition of O_2 leads to the formation of the carbonyl. Instability of the double bond after formation of the carbonyl may lead to the loss of the $CH_3(C{=}O)C(\bullet)H$ radical. This radical can then react with O_2 to eventually form methylglyoxal.

Oxime at 26.6 min [3-(1-hydroxy-1-methylethyl)-6-methylcyclohex-2-en-1-one]

This product was only observed as α-terpineol surface reaction product. This product was observed in all experiments where α-terpineol was applied to glass or vinyl when air or O_3 was present. The 26.6 min oxime was observed in the background of blank experiments with the α-terpineol solution; however, emission profile data also demonstrated this product being formed as a result of reaction over time (see Figure 2c). Interestingly, this product was not observed in any of the gas-phase experiments. A proposed mechanism for this product is challenging because there appears to be multiple reaction pathways for formation. Experiments indicated that the formation of the 26.6 min oxime may be explained by a combination of α-terpineol reaction on either glass or vinyl, O_3 reaction with α-terpineol and/or α-terpineol–water reactions on the surface.

This product showed an affinity for both the vinyl and glass surfaces unlike the 19.6 and 20.9, 21.6 and 21.9 min oximes (Table 3b). Interestingly, this product showed a different trend in its emission in the α-terpineol/glass/O_3 switch to air experiments. The 26.6 min oxime did not disappear immediately when O_3 was removed as was observed in the 19.6 and 20.9, 21.6, and 21.9 min oximes. Instead there was a slight decrease in the emission until approximately 36 h, then plateaued during the 36–72 h samples.

Conclusions

Using the FACS to accurately dope O_3 onto a surface that has been coated with a specific chemical is a unique approach to quantifying the influence a surface has on the indoor environment. It is evident that the surface in which a particular VOC is applied affects the formation of reaction products (e.g. formation of 20.9, 21.6 and 21.9 min oxime) and their emissions. The differences in the gas-phase measurements vs. the surface-phase measurements could be due to a number of factors such as: (i) relative humidity <10% (gas-phase) and 50% (surface-phase), (ii) VOC/O_3 reactions on FLEC surface, (iii) hydroxyl radical mediated reactions because of surface, (iv) steric hindrance effects as a result of orientation of VOCs to the surface and (v) surface enhanced reaction product formation.

The relative humidity has been shown to be a significant factor in observed gas-phase reaction chemistry. Recently, Jonsson et al. have observed the reaction of terpenes (such as: limonene, Δ^3-carene and α-pinene) with O_3 at higher humidities produced more low volatility products (Jonsson et al., 2006). This may explain the formation of 26.6 min oxime in surface-phase measurements (relative humidity% = 50%) and not in the gas-phase measurements (relative humidity < 10%). Further investigations of the dependence of the α-terpineol/O_3 surface-phase chemistry on humidity are needed.

The inner surface of the FLEC is made of hand-polished stainless steel with a Roughness great number less than 0.1 μm which minimizes the amount of sorption to the surface (Wolkoff, 2001). However, FLEC surface-phase chemical reactions still may occur, because stainless steel is porous and may harbor water or any of the emitted VOCs from the surface (Gandar and Tanner, 1976; O'Hanlon, 2003). Experiments were conducted with α-terpineol + O_3 for 12 h on vinyl, then switch to 'clean' glass. These results demonstrated that no reactions seem to occur on the FLEC surface.

Orientation of VOCs to the surface can significantly affect kinetics and observed reaction chemistry. Provided there is sufficient access, O_3 will react with the carbon–carbon double bond of alkenes to form energy rich Criegee biradicals (Kroll et al., 2001, 2002). If the carbon–carbon double bond is locked in a position that makes it unavailable for O_3 reaction, then a number of products may not be formed. However, in some cases, the VOC may be locked in a position that favors the O_3 reaction. For example, if the OH group of α-terpineol orients itself perpendicular to the surface, then the carbon–carbon double becomes more accessible to O_3 reaction. This may explain why the 20.9, 21.6 and 21.9 min oxime were observed in much larger yields than in the gas-phase measurements. This may also explain why the 26.6 min oxime was observed.

Comparison of the gas-phase and surface-phase reaction product yields based on chromatographic peak area gives insight to surface/VOC/O_3 interactions. For example, in the gas-phase experiments, methylglyoxal was the predominant reaction product that was observed. However, in the surface-phase experiments, the 19.6, 20.9, 21.6 and 21.9, and 26.6 min oximes were dominant. As mentioned above, this contrast may be due to relative humidity, α-terpineol concentration or other factors. One possibility may be the interaction between the energy rich intermediates and the surface which can lead to the stabilization of the higher molecular weight species. Once stabilized, these products can be subsequently emitted from the surface.

Determining the impact both gas-phase and surface-chemistry has on the indoor environment is important in evaluating occupant exposures. Previous gas-phase measurements of α-terpineol + O_3 showed the formation of a number of oxygenated organic products which have the potential to induce a respiratory response. However, surface-phase experiments showed that these oxygenated products were generated in different yield ratios than those observed in the gas-phase. Additionally, one surface-enhanced oxygenated organic product was observed. The choice of the surface in which a VOC is applied is critical in understanding the impact of indoor environmental chemistry. It is expected that materials with a more rugged surface morphology or porosity (i.e. used flooring tile, gypsum or particles board, carpet) may impact these reactions to a larger extent. The orientation of a particular VOC to a specific surface will also likely affect the indoor environment by influencing the reaction kinetics and product formation/emission. Further studies of the gas-phase and surface-phase chemistry of VOCs + indoor oxidant (OH, NO_3 or O_3) are needed.

Disclaimer

The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the Centers for Disease Control and Prevention/National Institute for Occupational Safety and Health.

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