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Surface chemistry of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone on silanized glass, glass, and vinyl flooring tiles

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ABSTRACT

The surface-phase reaction products of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) with ozone (O_3), air, or nitrogen (N_2) on silanized glass, glass and vinyl flooring tile were investigated using the recently published FACS (FLEC (Field and Laboratory Emission Cell) Automation and Control System). The FACS was used to deliver ozone (100 ppb), air, or N_2 to the surface at a specified flow rate (300 mL min^{-1}) and relative humidity (50%) after application of a 2.0% dihydromyrcenol solution in methanol. Oxidation products were detected using the derivatization agents: *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) and *N*,*O*-bis(trimethysilyl)trifluoroacetamide (BSTFA). The positively identified reaction products were glycolaldehyde, 2,6-dimethyl-5-heptenal, and glyoxal. The proposed oxidation products based on previously published VOC/O_3 reaction mechanisms were: 2,6-dimethyl-4-heptenal, 6-methyl-7-octen-2-one and the surface-specific reaction products: 6-methyl-6-hepten-2-one, 6-methyl-5-hepten-2-one, and 6-hydroxy-6-methylheptan-2-one. Though similar products were observed in gas-phase dihydromyrcenol/O_3 reactions, the ratio, based on peak area, of the reaction products was 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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1. Introduction

Cleaning and room deodorizing are common activities that can introduce a number of volatile organic compounds (VOCs) and semi-VOCs into the indoor environment. Application of these chemicals leads to diffuse gas-phase “clouds” and/or adsorption to surfaces also present indoors. These compounds can then react both in the gas phase and/or on surfaces with indoor oxidants such as hydroxyl radicals ($OH^•$), nitrate radicals ($NO_3^•$), and ozone (O_3). These oxidation reactions generate a variety of products such as aldehydes (e.g. formaldehyde), ketones, dicarbonyls (e.g. glyoxal, methylglyoxal, 4-oxopentanal), carboxylic acids, and organic nitrates (Atkinson et al., 1995; Espada et al., 2005; Forester et al., 2007; Weschler, 2001).

The gas-phase reactions of VOCs and semi-VOCs with the indoor oxidant ozone have been studied extensively; however, equivalent reactions with these compounds on variety of surfaces are limited (Ham and Wells, 2008; Moise and Rudich, 2002; Pandrangi and Morrison, 2008; Voges et al., 2007; Wells et al., 2008). Recently, Wells et al. investigated the surface reaction of O_3 with the highly unsaturated non-volatile alkene, squalene (found at levels of 5–15% of skin oil) (Wells et al., 2008). Squalene was applied to a glass surface and reacted with 100 ppb of O_3 resulting in the formation of the emitted gas-phase and surface-bound products of 6-methyl-5-hepten-2-one (6MHO), glyoxal, 4-oxopentanal, and geranyl acetone, consistent with previous observations (Coleman et al., 2008; Fruekilde et al., 1998; Weschler et al., 2007; Wisthaler et al., 2005). Voges et al. also did surface experiments with the atmospheric terpene, menthenol, on a glass plate with O_3 (Voges et al., 2007). 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 is greatly enhanced 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.

Understanding the transformations of VOC in the surface/VOC/O_3 system has implications in indoor occupant exposure assessment. Accurate exposure assessments rely on the ability to identify and quantify chemicals in the occupant environment. Indoor

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surface chemistry could be an unrecognized source of both expected and new oxygenated organic compounds in the indoor environment. Exposure to these oxygenated organic compounds could result in health effects. Recently, both glyoxal and methylglyoxal, observed oxygenated reaction products of VOC/oxidant chemistry, have been identified as sensitizers using local lymph node assay and QSAR modeling (Anderson et al., 2007). Understanding the formation of oxygenated reaction products by identifying emissions from the surface/VOC/O_3 system could provide useful insight into improving indoor air quality.

Dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) is a prevalent chemical used in both surface cleaning and room deodorizing products. It is also the lavender scent used primarily in soap fragrances and as a powerful supporting note in citrus and lime-type perfumes (Lyondell, 2008). The gas-phase reactions of dihydromyrcenol with both $OH^{\bullet}$ and O_3 have been reported (Forester et al., 2006). Interestingly, the measured rate constant of dihydromyrcenol + O_3 was much slower than expected. It was hypothesized that the long aliphatic chain of dihydromyrcenol which has a carbon–carbon double bond and OH functional group at opposite ends may interact by folding in the gas phase; hence inhibiting the ozone reaction. Assuming the OH functional group orients to the surface as suggested by Voges et al., then the ozone reaction may be enhanced leading to the formation of newly emitted oxidation products (Voges et al., 2007). The goals of the experiments (described below) are to identify the products from the reaction of O_3 and dihydromyrcenol on glass, silanized glass, and vinyl surfaces and qualitatively assess the emission pattern and compare against those for gas-phase reactions.

2. Experimental methods

2.1. FLEC Automation and Control System (FACS)

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.

2.2. Surface application of dihydromyrcenol

Dihydromyrcenol 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, silanized glass, or vinyl floor tile (urethane finish side up) for each of the experiments below. All experiments were done at room temperature, 22 ± 2 °C. An aluminum plate, with a 14.9 cm diameter hole in the center, was used as a template for spraying the surface (i.e., silanized glass, glass or vinyl). This insured that the area sampled was directly under the FLEC and that no detectable emissions were collected due to slowly evaporating solvent under the FLEC o-ring.

Before application of the dihydromyrcenol 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^{-1} 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^{-1} for 45 min. Several background experiments with only air flowing through the FLEC showed no emission products after ventilation, compared to new "non-ventilated" tiles where air only was present (Ham and Wells, 2008). Similar experiments with a "clean" glass or silanized glass tile also showed no emission products. Immediately following the ventilation step, the tile was sprayed and placed under the FLEC.

2.3. Materials

Dihydromyrcenol (99%), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%), *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (99+%), 2,6-dimethyl-5-heptanal (80%), 6-methyl-5-hepten-2-one (99%) and acetonitrile (ACN) (≥99.93%) were purchased from Sigma–Aldrich (St. Louis, MO). Methanol (high-performance liquid chromatography grade) and methylene chloride (Optima) were purchased from Fisher Scientific (Pittsburgh, PA). Ultra-high purity nitrogen (UHP N_2) was purchased from Butler Gas (McKees Rocks, PA). Heat-resistant borosilicate glass plates (25.4 cm × 25.4 cm × 0.32 cm) were purchased from McMaster-Carr (Atlanta, GA). Two of these borosilicate glass plates were then sent to Restek (State College, PA) to be coated with Siltek® to ensure the surface to be chemically inert. 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.

2.4. Dihydromyrcenol + air or N_2 on glass, silanized glass, or vinyl tile (FACS)

For the dihydromyrcenol/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^{-1}. During N_2 only experiments, a UHP N_2 tank was connected to FACS inlet.

2.5. Dihydromyrcenol + O_3 on glass, silanized glass, vinyl 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 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.

2.6. Dihydromyrcenol + O_3 on glass, silanized glass, or vinyl tile for 12 h, then switch to air for remainder (FACS)

In this experiment, the FACS was initialized using the same parameters as above. A glass, silanized glass, or vinyl tile was sprayed with the dihydromyrcenol solution described above, then placed under the FLEC. After 12 h, the ozone concentration was set to zero and just humidified air was allowed to flow through the system for the remaining 60 h of sampling.

2.7. Dihydromyrcenol + O_3 in an impinger

Experiments were conducted to determine if any of the products observed in surface-phase reactions were generated from dihydromyrcenol reacting with O_3 in the impinger. A dihydromyrcenol solution was prepared with 5 μL of 99% dihydromyrcenol mixed with 14.7 mL of methanol and placing in one of the 100 mL glass impinger used in 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^{-1} and relative humidity = 50%. After 12 h, the sample was collected, derivatized and analyzed, as described below. Experiments were also done with air flowing through the FLEC at 300 mL min^{-1} at 50% RH over 12 h.

2.8. Dihydromyrcenol + O_3 in a Teflon chamber

Experiments were conducted to determine if any of the products generated from surface-phase reactions would be observed in the gas phase. Dihydromyrcenol (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, ozone (approximately 100 ppb) was injected into the reaction chamber using a gas-tight syringe. These concentrations were based on previous indoor environment research (Singer et al., 2006; Wainman et al., 2000; Weschler, 2000). Two experimental reaction sets were collected approximately 20 min after O_3 injection. One reaction set consisted of a reaction chamber sample without ozone and a reaction chamber sample after ozone addition. The other reaction set was the same as above except cyclohexane (approximately 266 ppm) was added to the reaction mixture to scavenge OH. Approximately 20 L samples of the chamber contents were collected at ca. 3–4 L min^{-1} through a 100 mL impinger (p/n 652650-2440, Kontes, Vineland, NJ) filled with 3 mL of 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 conducted in duplicate.

2.9. Glass, silanized glass, or vinyl tile – rinse experiments

A series of rinse experiments were conducted by placing a glass, silanized glass, or vinyl tile (coated/uncoated with dihydromyrcenol) under the FLEC and then exposing with O_3 (100 ppb in air) or air for 72 h (see Table 1). After exposure, glass, silanized glass, or vinyl tiles were rinsed with 6 mL of HPLC grade methanol into a custom pyrex container (Ham and Wells, 2008). The rinsate was then collected and split into 2 vials. The first vial contained 1.5 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 for reaction completion.

2.10. Sample collection and analysis

Emissions from dihydromyrcenol reactions (FACS) were collected in a 100 mL glass impinger immersed in a thermostated 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, the output flow was switched to another impinger filled with 14.7 mL of methanol using a new computer controlled system so as to minimize the interruption to flow in the system. This multiple impinger system holds six 100 mL glass impingers in the 0 ± 0.5 °C bath which are connected in parallel with 0.64 cm ID Teflon tubing separated using Teflon solenoids (p/n 7911K12, McMaster-Carr, Atlanta, GA). This process was repeated until 72 h of total sampling was obtained for a total of six samples.

Table 1
Experimental list of rinse experiments.

	Surfaces	Reactant	Notes
1	Silanized Glass Vinyl	Air	Tile rinsed after 72 h under FLEC
2	Silanized Glass Vinyl Glass	N_2	Tile rinsed after 72 h under FLEC
3	Silanized Glass Vinyl	O_3, 100 ppb	Tile rinsed after 72 h under FLEC
4	Silanized Glass Vinyl Glass	O_3/Air	Tile rinsed after O_3 (100 ppb) for 12 h, then air for 60 h under FLEC

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 (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 done to monitor the concentration of dihydromyrcenol 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 derivatization 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) 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. 1 μL 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^{-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 to 650. Each sample was analyzed in duplicate. Acetonitrile was the chemical ionization reagent used for all CI spectra. Commercially available samples of the identified products (glycolaldehyde, 2,6-dimethyl-5-heptenal, and glyoxal) were derivatized and subsequently analyzed to verify matching ion spectra and chromatographic retention times.

3. Results

3.1. Observed reaction products

Derivatization of nonsymmetric carbonyls using PFBHA or PFBHA/BSTFA 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 dihydromyrcenol + 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). All observed reaction product information for both FACS and rinse experiments are described in Table 2. A summary table comparing the products observed from the FACS experiments is shown in Table 3.

To address possible oxidation reactions occurring in the impinger, experiments were conducted with dihydromyrcenol added directly to the impinger and exposed to O_3 for 12 h which resulted in the observation of all the reported reaction products; except the 14.3, 14.5, and 14.7 min peaks. However, the detection of these and other reaction products in 24–72 h surface chemistry experiments cannot be explained by oxidation reactions occurring in the impinger. Since the measured dihydromyrcenol concentration in the impinger during surface-phase experiments decreases to <1% of its maximum after 12 h, and a fresh impinger solution is inserted every 12 h, it is evident that the dihydromyrcenol 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, Fig. 2) were determined by integrating the peak area of the emission product at each of the 12 h sampling times. Duplicate experiments of these emission profiles are also shown in Fig. 2.

3.1.1. Dihydromyrcenol at retention time 6.8 min

Dihydromyrcenol was observed in all FACS experiments from all 1B vials where dihydromyrcenol was sprayed onto a glass, silanized glass, or vinyl tile. No dihydromyrcenol was observed in any of the rinse experiments.

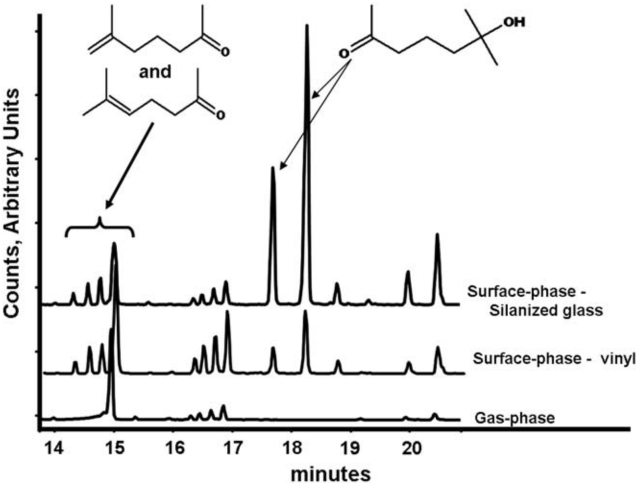


Fig. 1. Representative chromatograms of derivatized products of dihydromyrcenol + O_3 on silanized glass at 50% relative humidity (top), a vinyl tile (middle), and a gas-phase sample. Chromatograms are offset for clarity.

3.1.2. Glycolaldehyde ($HC({=}O)CH_2OH$)

Glycolaldehyde was observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, and dihydromyrcenol/O_3/silanized glass/cyclohexane. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl, but only in the first 12 h of sampling. Samples taken between 12 and 72 h showed no emission of glycolaldehyde.

3.1.3. Oximes at retention times (14.3 and 14.7 min) (6-methyl-6-hepten-2-one) and (14.5 and 14.9 min) (6-methyl-5-hepten-2-one, 6MHO)

The 14.3–14.9 min oximes were observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, and dihydromyrcenol/O_3/silanized glass/cyclohexane. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl, but only in the first 12 h of sampling. Samples taken between 12 and 72 h showed no emission of this product.

3.1.4. Oxime at retention times 16.3 and 16.6 min (2,6-dimethyl-6-heptenal) and (16.5 and 16.8 min) (2,6-dimethyl-5-heptenal)

The 16.3–16.8 min oximes were observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, and dihydromyrcenol/O_3/Teflon bag. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl, but only in the first 12 h of sampling. Samples taken between 12 and 72 h showed no emission of this product.

3.1.5. Oxime at retention time 17.6 and 18.2 min (6-hydroxy-6-methyl-2-heptanone)

The 17.6 and 18.2 min oximes were observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, and dihydromyrcenol/O_3/silanized glass/cyclohexane. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl, but only in the first 12 h of sampling. Samples taken between 12 and 72 h showed no emission of this product.

3.1.6. Oxime at retention time 19.9 and 20.4 min (6-methyl-7-octen-2-one)

The 19.9 and 20.4 min oximes were observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, dihydromyrcenol/O_3/Teflon bag, and dihydromyrcenol/O_3/silanized glass/cyclohexane. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl, but only in the first 12 h of sampling. Samples taken between 12 and 72 h showed no emission of this product.

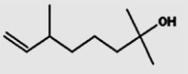
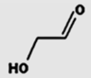
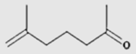
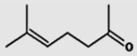
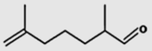
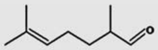
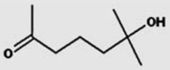
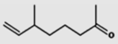
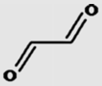
3.1.7. Glyoxal (ethanedial, $HC({=}O)C({=}O)H$)

Glyoxal was observed in the following experiments (Table 3): dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/O_3/vinyl, dihydromyrcenol/O_3/glass, dihydromyrcenol/O_3/Teflon bag, and dihydromyrcenol/O_3/silanized glass/cyclohexane. This product was also observed in dihydromyrcenol + O_3 for 12 h switch to air on silanized glass, glass, and vinyl. Glyoxal was observed in the 12–24 h sampling and 24–36 h sampling, but no emission was observed after 36 h.

3.2. Emission profiles

Emission profiles were determined by integrating the peak areas of the emission products at each of the 12 h sampling intervals. Example emission profiles of the surface-dependent oxidation

Table 2
List of observed reaction products of dihydromyrcenol + O_3 on silanized glass, glass, and vinyl.

Retention Time (min)	Name	Molecular Weight (amu)	EI ions Observed	CI ions observed
6.8	 dihydromyrcenol	156	43, 59, 67, 83, 95, 123	No CI ions were observed
10.1 10.4	 glycolaldehyde [a]	60	181, 195, 226, 238	256
14.3 14.7	 6-methyl-6-hepten-2-one	126	42, 72, 125, 181, 195, 322	322
14.5 14.9	 6-methyl-5-hepten-2-one	126	41, 67, 82, 181, 195, 322	322
16.3 16.6	 2,6-dimethyl-6-heptenal	140	81, 154, 181, 195, 253, 266, 336	336
16.5 16.8	 2,6-dimethyl-5-heptenal [a]	140	41, 72, 154, 181, 253, 336	336
17.6 18.2	 6-hydroxy-6-methyl-2-heptanone	144	43, 59, 82, 140, 181, 264, 280, 266, 322, 340	340
19.9 20.4	 6-methyl-7-octen-2-one	140	43, 59, 114, 138, 154, 181, 253, 266, 336	336
24.2 24.5	 glyoxal [a]	58	181, 195, 448	449

products (14.7 min, 18.2 min, and the 20.4 min oximes) are illustrated in Fig. 2. All reaction products showed longer emission times on vinyl surfaces compared to both glass and silanized glass. Specifically the oximes at 16.3, 16.5, 16.6, and 16.8 had the longest emission times with products being emitted after 72 h of sampling on vinyl. Interestingly, glycolaldehyde, 14.3, 14.5, and 14.7 min oximes had an emission max at 24 h instead of 12 h on vinyl. It is possible that the OH group of glycolaldehyde makes it more likely to adsorb to the surface thus preventing emission in the first 12 h. This may also occur with the carbonyl group of the smaller molecular weight species such as the 14 min oximes. This result may also suggest that these products are secondary products formed after substantial generation of a primary oxidation product and subsequent reaction with O_3 or other radical driven process. All samples of dihydromyrcenol + O_3 on both glass and silanized glass showed no emission of any oxidation products after 24 h.

Oximes at 17.6, 18.2, 19.9, 20.4, and glyoxal had the shortest overall emissions on all surfaces. The highest observed concentration was observed at 12 h and rapid decrease to <10% in the 24 h samples and <0.5% in the 72 h samples.

3.3. *Rinse experiments*

After 72 h experiments with dihydromyrcenol on a surface, the glass, silanized glass, or vinyl was rinsed with methanol to determine if any residual oxidation products were on the surface. The 17.6 and 18.2 min oxime was only observed in rinsing after the dihydromyrcenol/O_3/silanized glass experiment. The 19.9 and

Table 3
Comparison of products observed in dihydromyrcenol + O_3/air on silanized glass, glass, or vinyl.

	Chromatographic Retention Time of Products (min)							
	Glycolaldehyde	14.3 14.7	14.5 14.9	16.3 16.6	16.5 16.8	17.6 18.2	19.9 20.4	Glyoxal
FACS Experiments								
DHM/Silanized Glass/Air	○	○	○	○	○	○	○	○
DHM/Silanized Glass/N_2	○	○	○	○	○	○	○	○
DHM/Silanized Glass/O_3	●	●	●	●	●	●	●	●
DHM/Vinyl/Air	○	○	○	○	○	○	○	○
DHM/Vinyl/N_2	○	○	○	○	○	○	○	○
DHM/Vinyl/O_3	●	●	●	●	●	●	●	●
DHM/Glass/N_2	○	○	○	○	○	○	○	○
DHM/Glass/O_3	●	●	●	●	●	●	●	●
DHM/Silanized Glass/O_3/cyclohexane	●	●	●	○	○	●	●	●
DHM/Teflon Bag/O_3/cyclohexane	○	○	○	●	●	○	●	●

20.4 min oxime was only observed after rinsing in the dihydromyrcenol/air/vinyl experiment. Glyoxal was observed in the following rinse experiments: dihydromyrcenol/air/silanized glass, dihydromyrcenol/O_3/silanized glass, dihydromyrcenol/N_2/silanized glass, dihydromyrcenol/air/vinyl, dihydromyrcenol/O_3/vinyl, and dihydromyrcenol/N_2/glass.

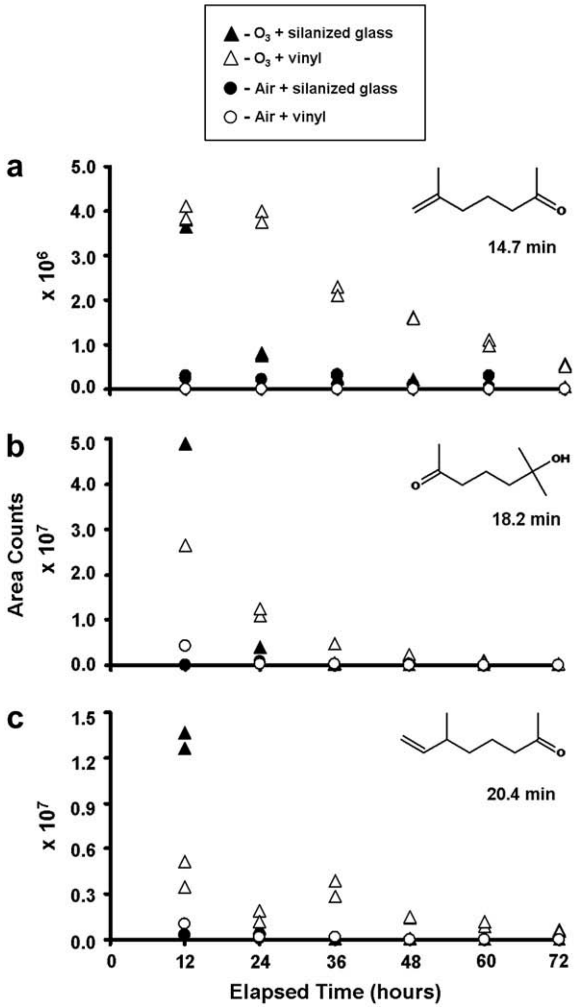


Fig. 2. Emission profiles of dihydromyrcenol + O_3 or air proposed reaction products on silanized glass or vinyl (FACS experiments). (a) 6-Methyl-6-hepten-2-one (14.7 min), (b) 6-hydroxy-6-methyl-2-heptanone (18.2 min), (c) 6-methyl-7-octen-2-one (20.4 min).

4. Discussion

The gas-phase kinetics and reaction products of dihydromyrcenol with the hydroxyl radical ($OH^•$) and ozone has been studied previously (Forester et al., 2006). Ozone was estimated to react with the carbon–carbon double bond of dihydromyrcenol with an upper limit determined rate constant of 2×10^{-18} cm^3 $molecule^{-1}$ s^{-1} which is approximately 6 times slower than the calculated dihydromyrcenol/O_3 rate constant of 1.2×10^{-17} cm^3 $molecule^{-1}$ s^{-1} using Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91 (EPA, 2000). This difference in rate constants was unexpected and suggests that the ability of ozone to add to the carbon–carbon double bond of dihydromyrcenol is reduced by either steric hindrance or reduced electron density or both. The results of dihydromyrcenol/O_3 surface experiments clearly demonstrate the formation and subsequent emission of reaction products not observed in the dihydromyrcenol/O_3 gas-phase experiments (Fig. 1).

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 dihydromyrcenol + O_3. Based on the reaction rate constant determined previously of $k_{\text{dihydromyrcenol}+O_3} = 2 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} and an $[O_3] = 100$ ppb, a pseudo-first order reaction rate of 0.02 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^{-1}, 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. Additionally, the higher exchange rate inherent with using the FLEC is not a great concern, since the velocity across the surface approximates what is found indoor environments (Wolkoff, 2001).

The significant products, based on chromatographic peak areas, reported from the dihydromyrcenol/O_3 gas-phase reactions were: 2-methylpropanal, 2-methylbutanal, 2,6-dimethyl-5-heptenal, glyoxal, and methylglyoxal (Forester et al., 2006). Below are possible mechanistic explanations of the observed products from dihydromyrcenol/O_3 surface-phase experiments. These reactions may occur in parallel.

4.1. Glycolaldehyde (HC(=O)CH_2OH) and oximes at retention times 14.3 and 14.7 min (6-methyl-6-hepten-2-one) and 14.5 and 14.9 min (6-methyl-5-hepten-2-one)

The glycolaldehyde and 14 min oximes were observed from all FACS experiments as a reaction product of the dihydromyrcenol/O_3 surface reaction. These products were also observed in dihydromyrcenol/O_3/Teflon bag gas-phase experiments, except when cyclohexane was added to the reaction mixture. Cyclohexane actively scavenges OH radicals formed from alkene/O_3 reactions when its concentration is at least double that of ozone (Kroll et al., 2001, 2002). Surface-phase experiments were done with continuous injection of 500 ppb of cyclohexane into the FACS air flow over 72 h; however, glycolaldehyde and the 14 min oximes were still observed. This result suggests that OH radical formation and subsequent reaction with dihydromyrcenol is unlikely. A possible mechanism for the formation of glycolaldehyde and the 14 min oximes is shown in Fig. 4. The formation of the "folded" primary ozonide with subsequent loss of the ethylene ozonide and alcoholic OH could result in the formation of glycolaldehyde and the ketone/alkene products 6-methyl-6-hepten-2-one and 6-methyl-5-hepten-2-one (oximes observed at 14.3–14.9 min). This reaction pathway is further supported by observing that the glycolaldehyde emission profile (not shown) closely matches the surface-specific emission profiles attributed to 6-methyl-6-hepten-2-one and 6-methyl-5-hepten-2-one, Fig. 2.

4.2. Oximes at retention time 16.3 and 16.6 min (2,6-dimethyl-4-heptenal) and 16.5 and 16.8 min (2,6-dimethyl-5-heptenal)

Both 2,6-dimethyl-4-heptenal and 2,6-dimethyl-5-heptenal were observed in all dihydromyrcenol/O_3 surface-phase experiments. Analogous to the 14 min oximes, two distinct compounds were observed over this chromatographic retention time range, and it is apparent that they have very similar structures. As was seen with the formation of the 14 min oximes, the 16 min oximes can be generated by ozone addition to the carbon–carbon double bond forming the ozonide with subsequent folding of dihydromyrcenol, as described above (Fig. 4). Again, folding leads to an interaction between the ozonide and the terminal OH group. This results in the formation of the $CH_2^{\bullet}CH(CH_3)(CH_2)_3(C^{\bullet})(CH_3)_2$ biradical by loss of the alcoholic OH with simultaneous removal of the ozone/methylene moiety. The CH_2 radical can add oxygen, form a Criegee biradical and then stabilize to a carbonyl (Atkinson, 1997; Atkinson and Arey, 2003). As described for the 14 min products above, the carbon radical with two methyl groups attached can form a carbon–carbon double bond with one of the terminal methyl groups losing hydrogen or can form a carbon–carbon double bond with the neighboring methylene group in the carbon chain. Both of these products have similar surface-specific emission profiles in which a larger initial emission is observed from the glass surfaces with decays in the next 12 h and detectable emissions from vinyl even after 60 h. Like the reaction products observed from 14.3 to 14.9 min, there is a steady emission for the first 36 h of the experiment and then a decay to near zero at 72 h.

4.3. Oxime at retention time 17.6 and 18.2 min (6-hydroxy-6-methyl-2-heptanone)

As with the 14 min oximes, 6-hydroxy-6-methyl-2-heptanone was observed in all dihydromyrcenol/O_3 surface-phase experiments, but was not observed in any of the dihydromyrcenol/O_3/Teflon bag gas-phase experiments. The proposed mechanism for its formation is shown in Fig. 5. Ozone can add to the double bond with subsequent beta scission resulting in the formation of the $CH_3(C^{\bullet})(CH_2)_3C(CH_3)_2OH$ radical which can add oxygen leading to a peroxy radical. This radical can then form the corresponding carbonyl group by reaction with $R'O_2^{\bullet}$ (Fig. 5). This mechanism is further supported by the formation of glyoxal produced from the ozone/ethylene moiety generated after beta scission. This experimental evidence strongly suggests that the surface does have an influence on the chemistry of the dihydromyrcenol/O_3 system.

The emission profile of the 17.6/18.2 min oxime (Fig. 3) indicates a maximum occurring at 12 h with a rapid decay in the next 24 h (24 and 36 h samples).

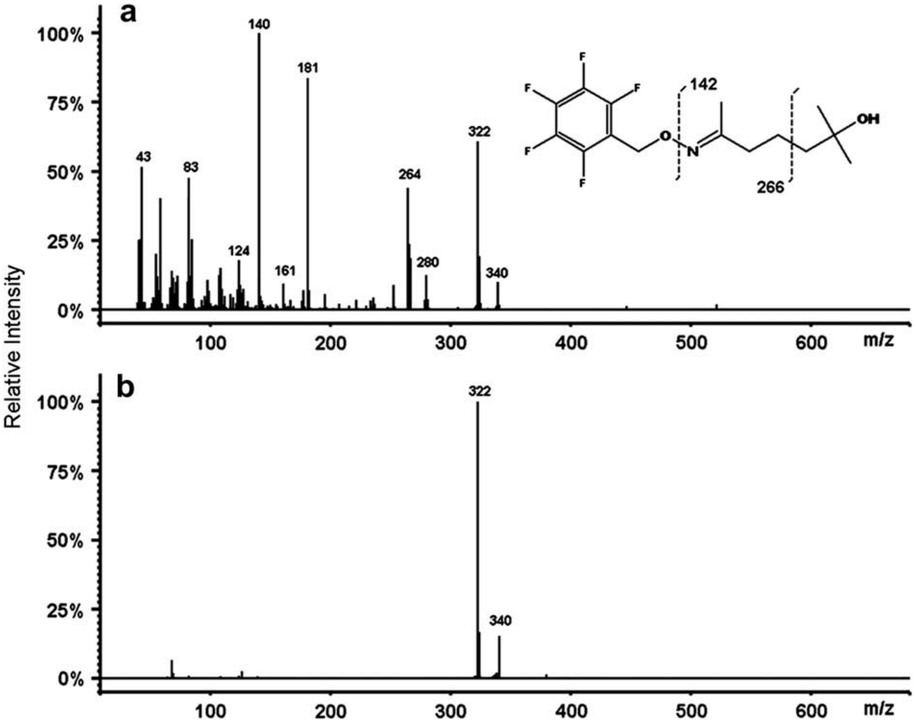


Fig. 3. Mass spectra of PFBHA-derivatized 6-hydroxy-6-methyl-2-heptanone (17.6 and 18.2 min). (a) EI mass spectrum, (b) CI mass spectrum using acetonitrile as chemical ionization reagent.

4.4. Oxime at retention time 19.9 and 20.4 min (6-methyl-7-octen-2-one)

6-Methyl-7-octen-2-one was observed in all surface and gas-phase experiments. The proposed mechanism is shown in Fig. 4. Similar to both the 14 and 16 min oximes, ozone adds to the carbon–carbon double bond forming the primary ozonide with subsequent folding leading to the close proximities of the ozonide and terminal OH. This interaction can lead to ejection of OH and ozone to produce the biradical, $(CH_2^{\bullet})CH_2CH(CH_3)(CH_2)_2(C^{\bullet})(CH_3)_2$. The carbon radical site with two methyl groups attached could add oxygen, form a Criegee biradical and then form the stable carbonyl with the loss of one of the methyl groups. The CH_2 radical on the other end of the molecule could form a carbon–carbon double bond. The emission profiles for this reaction product show an initial increase at 12 h and a rapid decay to baseline by the 24–36 h timeframe except for the slight increase observed in the dihydromyrcenol/O_3/vinyl experiments.

4.5. Glyoxal (ethanedial, HC(=O)C(=O)H)

Glyoxal was observed in both the surface and gas-phase experiments. Like the 17.6 and 18.2 min oxime, glyoxal is generated from ozone addition with subsequent beta scission resulting in the formation of the $CH_3(C^{\bullet})(CH_2)_3C(CH_3)_2OH$ radical and the Criegee radial, $CH(O)CH(^{\bullet})(OO^{\bullet})$, Fig. 5. This Criegee radical can react with $R'O_2^{\bullet}$ leading to the formation of glyoxal. The emission profile for glyoxal closely matches the 17.6 and 18.2 min product further supporting the proposed surface reaction mechanism. Glyoxal's emission profile was observed to peak in the first 12 h and then rapidly decay to near background levels by the 24 h sample.

5. Conclusions

The surface-phase experiments of dihydromyrcenol + O_3 on glass, silanized glass, and vinyl produced significantly different results compared to previously published gas-phase studies (Forester et al., 2006). Forester et al. observed two of the oxidation products reported here of 2,6-dimethyl-5-heptenal and glyoxal. However, the dihydromyrcenol + O_3 reaction on glass, silanized glass and vinyl generated newly observed surface-dependent proposed oxidation products of 6-methyl-6-hepten-2-one, 6-methyl-5-hepten-2-one, and 6-hydroxy-6-methyl-2-heptanone. The formation of these surface-unique products indicates that these types of oxidation reactions can be influenced by interactions with a surface. In summary, it was observed that reactions on

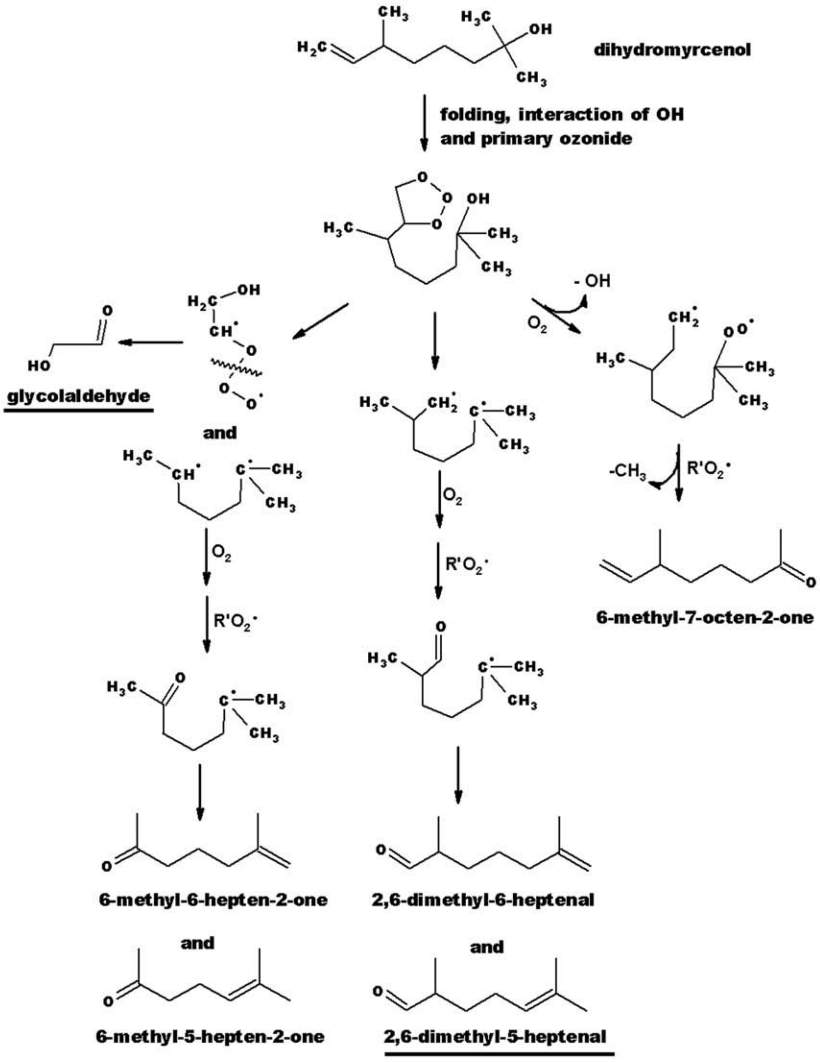


Fig. 4. Proposed mechanism for the formation of dihydromyrcenol + O_3 surface reaction products. Underlined names indicated positively identified products.

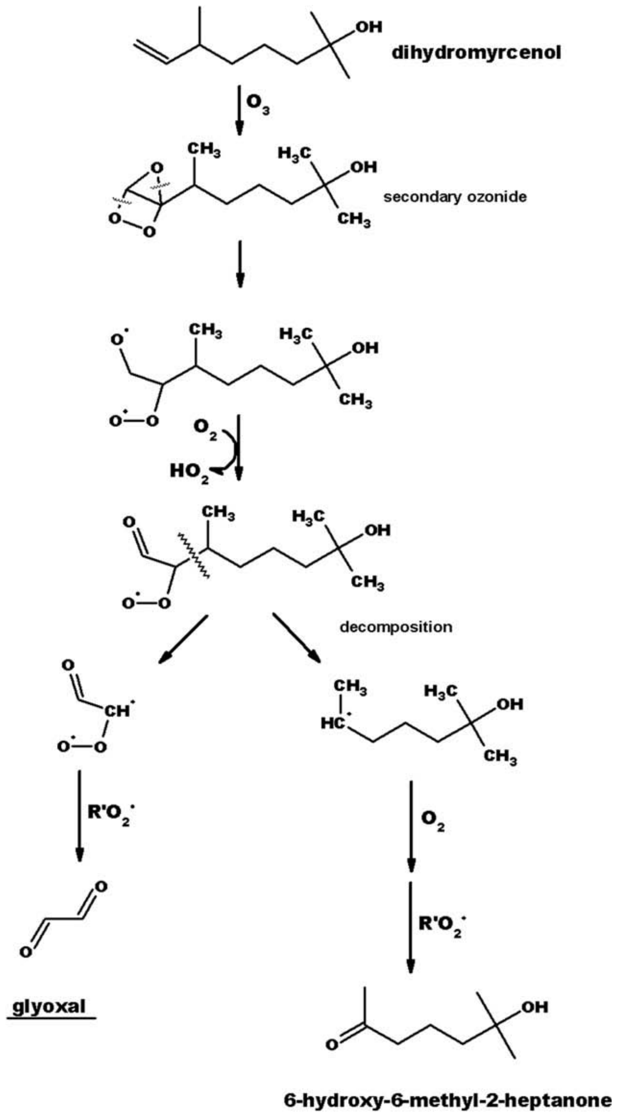


Fig. 5. Proposed mechanism for the formation of glyoxal and 6-hydroxy-6-methyl-2-heptanone (17.6 and 18.2 min) for the surface reaction of dihydromyrcenol + O_3. Underlined names indicated positively identified products.

silanized glass showed peak emissions which decreased significantly after 12 h. However, surface-phase reactions on vinyl showed product emissions over a longer period of time indicating absorption of dihydromyrcenol or reaction products.

Observation of these surface-unique products may be explained by the orientation of the alcoholic OH group of dihydromyrcenol to the surface. In previously published gas-phase experiments of dihydromyrcenol/O_3, an unexpectedly low rate constant was determined. It was hypothesized that since dihydromyrcenol has a long aliphatic chain which has a carbon–carbon double bond and an OH functional group at opposite ends that they could interact by molecular folding in the gas phase; hence inhibiting the ozone reaction. This folding could have an impact on the electron density of the carbon–carbon double bond as well as add steric hindrance. However it is plausible, that the OH group could be bound to the surface leaving the carbon–carbon double bond free to react with ozone leading to the formation of the newly observed products. Reorientation of the alcoholic functional group to the surface was previously proposed by Ham et al. after investigations of α-terpineol + O_3 on glass and vinyl (Ham and Wells, 2008). Recently, Voges et al. forced this orientation by affixing the OH functional group of the atmospheric terpene, menthenol, to a glass surface.

To quantify the reaction enhancement due to surface attachment, a comparison of the reaction probabilities between dihydromyrcenol/O_3 gas-phase and dihydromyrcenol/O_3 surface-phase kinetics is needed. The determination of the magnitude of surface enhanced reaction has been previously assessed for the squalene/O_3, oleic acid/O_3, linoleic acid/O_3, soiled clothing and hair systems (Coleman et al., 2008; Moise and Rudich, 2002; Pandrangi and Morrison, 2008; Wells et al., 2008). Additionally, Voges et al. investigated the interaction of surface-bound menthenol with ozone on glass. In these experiments, menthenol was oriented so that the OH group was bound to the glass surface by silane-functionalization chemistry. The surface-bound reaction probabilities were observed to increase between 5 and 20 times when compared with gas-phase reaction probabilities (Voges et al., 2007). The volatility of dihydromyrcenol complicates the ability to assess the surface enhancement of the dihydromyrcenol/O_3 reaction from the experimental data presented above. Experiments in which the dihydromyrcenol molecule is affixed to the surface utilizing an attachment technique or some other method of preventing dihydromyrcenol evaporation will be necessary to accurately determine a surface enhancement value for the dihydromyrcenol/O_3 reaction.

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