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Yields of Carbonyl Products from Gas-Phase Reactions of Fragrance Compounds with OH Radical and Ozone

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Chamber studies to quantify formation yields of oxygenated organic reaction products were performed for gas-phase reactions of the hydroxyl radical (OH•) and ozone (O_3) with the common cleaning product terpene compounds limonene, α-terpineol, and geraniol. The reaction products observed were identified and quantified using derivatization by *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and gas chromatography/mass spectrometry. Limonene rate constants and product mechanisms have been examined previously. Several of these investigations have measured product yields from limonene reactions and those results are compared with the results presented here. Although rate constants and product mechanisms have previously been investigated for α-terpineol and geraniol, yields of oxygenated organic reaction products have not been measured. Reactions from the fragrance compounds in this study produced several dicarbonyl reaction products such as glyoxal, methylglyoxal, and 4-oxopentanal which were observed from all three terpenes. Total carbonyl yields ranged from 5.1% for the limonene + O_3 reaction to 92% for the geraniol + O_3 reaction.

Introduction

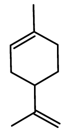
In a report released in October, 2007, the American Academy of Allergy Asthma & Immunology estimated that 15% (1 in 7) of adult-onset asthma cases in the United States are work-related resulting in 24.5 million missed workdays each year (*1*). Research has indicated that exposure to oxygenated organic compounds may cause adverse health effects and compounds with multiple oxygen groups such as dicarbonyls are implicated as possible respiratory sensitizers (*2*).

Workers at greater risk include approximately 4.2 million people in the U.S. employed as janitors and cleaners (*3*−*5*). Although many workplace injuries among this group are often unreported, twelve percent of those that are reported are associated with inhalation of fumes and respiratory problems. Using these statistics and the U.S. Occupational Safety and Health Administration's cost calculation worksheet, this translates to an estimated annual cost of over $800 million dollars to employers and employees combined (*6*).

Each of these workers uses an average of 23.2 gallons of cleaning and air freshening products annually and is therefore exposed to a wide variety of products that contain volatile organic compounds (VOCs) such as terpenes and terpene alcohols (*7*). When these products are applied, the emitted VOCs can react with initiator species present indoors such as ozone (O_3), hydroxyl radical (OH•), and nitrate radical (NO_3•). These reactions may occur either in the gas phase or on surfaces and produce a variety of oxygenated organic products including aldehydes, ketones, carbonyl and dicarbonyl species, and organic nitrate products.

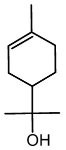
Limonene (Structure 1), is a cyclic terpene found in the rind of citrus fruits and is widely used as a solvent and/or odorant in many cleaning formulations. The annual worldwide production of d-limonene is approximately 75,000 tons and rising (*8*). Limonene ranks first in frequency among compounds used as fragrances in products used in domestic and occupational settings (*9*). Because it is ubiquitous, limonene's fate in the indoor environment has been previously assessed by investigating its reaction rate constants, product transformation mechanisms, and reaction product yields (*10*−*19*). Singer et al. investigated emission rates of various cleaning products and activities and for limonene in particular it was found that 7−70% of the limonene applied to surfaces can be emitted into the gas-phase (*20*). Although limonene is often detected in high concentrations through direct sampling and analysis in studies designed to assess indoor air quality (*21*), many of the gas-phase products from limonene + OH• and/or limonene + O_3 reactions are polar and difficult to detect directly using conventional sampling coupled with gas chromatography (*22*).

Structure 1: Limonene



Alpha-terpineol (Structure 2) is a terpene alcohol, a major component of pine oil, and is used widely in consumer products. The α-terpineol structure contains an endocyclic double bond comparable to that of limonene and its gas-phase reactions produce many of the same oxygenated organic products that are observed in gas-phase limonene reactions. The rate constants and product formation mechanisms with OH• or O_3 have been previously studied (*23*).

Structure 2: α-Terpineol



Geraniol (Structure 3) is a terpene alcohol with two carbon−carbon double bonds that is found naturally in rose scent and is also widely used in cleaning products. Geraniol ranks fourth in frequency among compounds used as fragrances in products designed for use in domestic and occupational settings (*9*). Gas-phase reactions of geraniol produce many of the same oxygenated organic products that are observed in gas-phase reactions of both limonene and α-terpineol. The rate constants and product formation mechanisms with OH• or O_3 have been previously studied (*24*).

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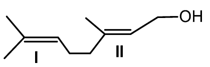
Structure 3: Geraniol



In this work, percent yields and carbon balances of carbonyls were determined from reactions of $OH\cdot$ or O_3 with limonene, α-terpineol, and geraniol using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) for derivatization of the carbonyl groups. The resulting oximes were analyzed and quantified using gas chromatography/mass spectrometry.

Experimental Methods

Apparatus and Materials. All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): glycolaldehyde dimer (100%), 6-methyl-5-hepten-2-one (99%), 5-hydroxy-2,5,6-trimethylheptan-3-one (~78%), 4-methylcyclohexanone (99%), dihydrocarvone (97%), carvone (99%), cyclohexane (99.9%), limonene (99%), geraniol (98%), α-terpineol (90%), *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%), glyoxal (40% in water), and methyl glyoxal (40% in water); from Fisher Scientific (Fairlawn, NJ): methanol (99%). 4-Oxopentanal (98%, 4-OPA) was synthesized by Richman Chemical Inc. (Lower Gwynedd, PA) according to Hutton et al. (*25*). Nitric oxide (99+% pure) was obtained as a 4942 ppm mixture in nitrogen from Butler Gases (Morrisville, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV) and used as received. Experiments were carried out at (297 ± 3) K and 1 atm pressure.

Hydroxyl radicals, which are among the oxidizing radicals in the indoor environment (*26*–*29*), were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air (*30*). CH_3ONO was prepared in gram quantities using the method of Taylor et al. (*31*) and stored in a lecture bottle at room temperature. Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon chamber and transferred using a gastight syringe. An additional port was added to the Teflon reaction chamber to facilitate the injection of ozone.

Identification of reaction products was made using PFBHA to derivatize carbonyl products (*22, 32*). Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in both the electron impact (EI) and chemical ionization (CI) modes (*22*). Compound separation was achieved by a Restek (Bellefonte, PA) Rtx-5MS (0.25 mm i.d., 30 m long, 1 μm film thickness) column.

Derivatized product samples were injected in the splitless mode, and the GC injector was returned to split mode one minute 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 (*22*). The following GC oven temperature parameters were used: 60 °C for 1 min then 20 °C/min to 170 °C, then 3 °C/min to 280 °C and held to the end of the chromatographic run. Underivatized parent samples were 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 170 °C/min to 250 °C and held to the end of the chromatographic run. The following GC oven temperature parameters were used: 60 °C for 1 min then 20 °C/min to 280 °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. 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.

Experimental Procedures. Twenty liters of chamber contents flowing at a rate of 2.5 L min^{-1} for 8 min was pulled through an impinger containing 3.6 mL of methanol using house vacuum and an MKS 5000 sccm flow controller (Andover, MA). One hundred microliters of impinger contents were removed after sampling and placed in an autosampler vial for quantification of the parent compound. One microliter of this solution was injected into the Varian 3800/Saturn 2000 GC/MS system. The remainder of the sample (approximately 1.6 mL) was removed from the impinger and 200 μL of 0.02 M PFBHA in acetonitrile was added to the contents to derivatize the carbonyl reaction products to oximes (*22*). The samples were allowed to react in the dark for 24–48 h. The reacted solutions were gently blown to dryness with UHP N_2, reconstituted with 100 μL of methanol, and then 1 μL of the reconstituted solution was injected into the Varian 3800/Saturn 2000 GC/MS system for quantification of the reaction products.

The concentrations of fragrance compounds injected into the Teflon chamber were consistent with concentrations typically found in the indoor environment after application and emission of a cleaning product (*9*).

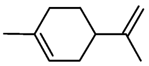
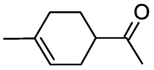
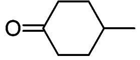
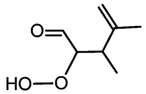
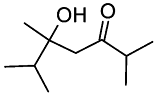
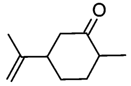
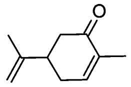
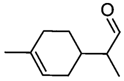
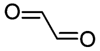
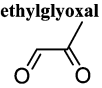
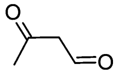
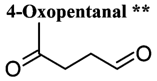
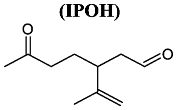
For the $OH\cdot$ experiments the typical concentrations of the pertinent species in the 85–115 L Teflon chamber were 0.6–1.0 ppm (1.5×10^{13} to 2.5×10^{13} molecule cm^{-3}) fragrance compound, 10 ppm (23×10^{13} molecule cm^{-3}) CH_3ONO, and 0.6 ppm (1.4×10^{13} molecule cm^{-3}) NO in air. Typically, three photolysis intervals of 5 s each were used on the reaction mixture for a combined total photolysis time of approximately 15 s and the final NO concentrations were ≥ 0.02 ppm ($\geq 5 \times 10^{11}$ molecule cm^{-3}). The total ion chromatogram (TIC) from the Saturn 2000 mass selective detector was used to identify products.

For the O_3 experiments, the typical concentrations of the pertinent species in the 85–115 L Teflon chamber were 0.6–1.0 ppm (1.5×10^{13} to 2.5×10^{13} molecule cm^{-3}) fragrance compound. The initial O_3 concentration in the absence of reactants was typically 0.05–0.1 ppm (4.9×10^{11} to 2.5×10^{12} molecule cm^{-3}). The concentration of O_3 was consistent with concentrations observed indoors and was the limiting reagent in the O_3 reactions. The gas-phase mixtures were allowed to react for at least 30 min after each addition of O_3. No steps were taken to prevent secondary reactions between O_3 and reaction products formed. Cyclohexane (288 ppm, 7.1×10^{15} molecules cm^{-3}) was added to the fragrance + O_3 reaction experiments to scavenge OH radicals (*33*). Typically, three additions of O_3 were added to the reaction mixture. The TIC from the Saturn 2000 mass selective detector was used to identify/quantify products.

Calibration curves consisting of 3–5 points were generated for each of the products observed. Commercially available reaction products were purchased and used for quantification. Many of the products observed were unique and unfortunately not available commercially and synthesis was not feasible. In these instances structurally similar surrogate compounds were used. A complete list of products and the surrogates used for calibration along with their structures may be found in Tables 1, 2 and 3. Possible chromatographic interferences were determined as described previously (*24, 34*).

All samples were quantified by integrating the area under the peak in the TIC chromatogram. The loss of the parent fragrance compound was plotted against the formation of products, generating a straight line with a slope equal to the product yield. The error in each yield value is the 95% confidence level (2 standard deviations) from the random uncertainty in the slope. Formation yield plots for limonene reactions may be viewed in Figure 1 and additional figures for α-terpineol and geraniol reactions may be viewed in the Supporting Information.

TABLE 1. Yields of Carbonyl Products from OH and O_3 Reactions with Limonene

Product name Structure	Hazard Index	% Yield OH	Carbon balance OH	% Yield O_3	Carbon balance O_3	Compound used for calibration
Limonene 	0.18					Limonene
4-Acetyl-1-methylcyclohexene (4AMCH) 	0.25	15	13	2.0	1.8	4-Methylcyclohexanone 
2-hydroperoxy-3,4-dimethyl pent-4-enal** 	0.30	ND	ND	2.3	1.6	5-Hydroxy-2,5,6-trimethyl-heptan-3-one 
Dihydrocarvone ** 	0.31	2.3	2.3	ND	ND	Dihydrocarvone
Carvone 	0.28	*	*	ND	ND	
2-(4-Methylcyclohex-3-en-1-yl)propanal ** 	0.66	2.3	2.3	ND	ND	Dihydrocarvone
Glyoxal 	0.66	0.5	0.1	0.4	0.1	Glyoxal
Methylglyoxal ** 	0.38	<0.4	<0.4	<0.4	<0.4	Methylglyoxal
3-Oxobutanal 	0.45	0.4	0.2	ND	ND	4-Oxopentanal
4-Oxopentanal ** 	0.52	0.4	0.2	<0.4	<0.4	4-Oxopentanal
3-Isopropenyl-6-oxoheptanal (IPOH) 	0.81	15	15	0.4	0.4	4-Oxopentanal
Total Yield		35.9%	33.1%	5.1%	3.9%	

* Product confirmed, unable to quantify due to chromatographic interference. ** Product unique to this study.

Because the reaction products could also react with residual OH· or O_3 in the reaction system, the observed product concentrations had to be corrected for these potential reactions. This correction has been described in detail (*35, 36*) and has the following form:

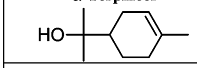
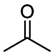
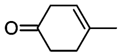
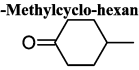
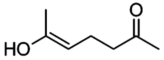
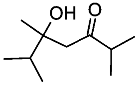
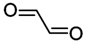
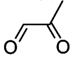
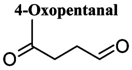
$$F=\frac{(k_{\mathrm{Fragrance}}-k_{\mathrm{P}})}{k_{\mathrm{Fragrance}}}\times\frac{1-\dfrac{[\mathrm{Fragrance}]_t}{[\mathrm{Fragrance}]_0}}{\left(\dfrac{[\mathrm{Fragrance}]_t}{[\mathrm{Fragrance}]_0}\right)^{k_P/k_{Fragrance}}-\dfrac{[\mathrm{Fragrance}]_t}{[\mathrm{Fragrance}]_0}} \tag{1}$$

F, the correction factor, was multiplied by the reaction product concentration data; $k_{\mathrm{Fragrance}}$ is the OH· or O_3 + Fragrance rate constant, and k_{P} is the rate constant for the reaction of OH· or O_3 with reaction product. The measured value for k_{P} was used when possible, but k_{P} was calculated using structure reactivity relationships (*37*) when no measured value was available in the literature. It should be noted that the observed reaction products exhibited linear concentration profiles even without the correction factor. The lack of curvature strongly suggests that no unusual side reactions generated or removed primary reaction products. The maximum correction factors may be viewed in Tables S1, S2, and S3 in the Supporting Information.

Results

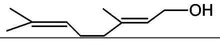
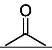
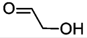
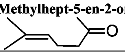
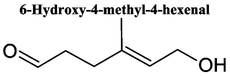
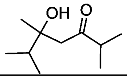
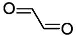
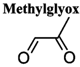
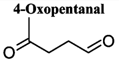
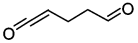
Limonene Results. Several studies have measured yields for limonene reactions with OH· or O_3. These previous studies

TABLE 2. Yields of Carbonyl Products from OH and O_3 Reactions with α-Terpineol

Product name Structure	Hazard Index	% Yield OH	Carbon balance OH	% Yield O_3	Carbon balance O_3	Compound used for calibration
α-Terpineol 	.15					α-Terpineol
Acetone 	0.07	*	*	ND	ND	
4-Methyl-3-cyclohexen-1-one 	0.16	5.7	4.0	ND	ND	4-Methylcyclo-hexanone 
6-Hydroxyhept-5-en-2-one 	0.13	20	14	31	21	5-Hydroxy-2,5,6-trimethyl-heptan-3-one 
Glyoxal 	0.66	1.4	0.3	ND	ND	Glyoxal
Methylglyoxal 	0.38	0.5	0.1	1.9	0.6	Methylglyoxal
4-Oxopentanal 	0.52	2.2	1.1	0.6	0.3	4-Oxopentanal
Total Yield		29.8%	19.5%	33.5%	21.9%	

* Product confirmed, unable to quantify due to chromatographic interference.

TABLE 3. Yields of Carbonyl Products from OH and O_3 Reactions with Geraniol

Name Structure	Hazard Index	% Yield OH	Carbon balance OH	% Yield O_3	Carbon balance O_3	Compound used for calibration
Geraniol 	0.15					Geraniol
Acetone 	0.07	*	*	*	*	
Glycolaldehyde 	0.14	29	5.7	31	6.2	Glycolaldehyde
6-Methylhept-5-en-2-one 	0.23	7.5	6.0	14	11	6-Methylhept-5-en-2-one
6-Hydroxy-4-methyl-4-hexenal 	0.39	ND	ND	26	18	5-Hydroxy-2,5,6-trimethyl-heptan-3-one 
Glyoxal 	0.66	0.5	0.1	0.6	0.1	Glyoxal
Methylglyoxal 	0.38	ND	ND	6.5	2.0	Methylglyoxal
4-Oxopentanal 	0.52	37	19	3.5	1.8	4-Oxopentanal
5-Oxopent-4-enal 	0.80	ND	ND	10	5.0	4-Oxopentanal
Total Yield		74.0%	30.8%	91.6%	44.1%	

* Product confirmed, unable to quantify due to chromatographic interference.

have used high-performance liquid chromatography (HPLC) with 2,4-dinitrophenylhydrazine (DNPH) (*14, 15*), liquid chromatography/mass spectrometry (LC/MS) (*13*), or gas chromatography with a flame ionization detector (GC-FID) (*16*). The results presented here focus solely on yields of carbonyl reaction products using PFBHA derivatization and GC/MS. Several of the reaction products listed in Table 1 have been observed in previous studies (*16*) however, reaction products were observed from both OH· and O_3 reactions that are unique to this study.

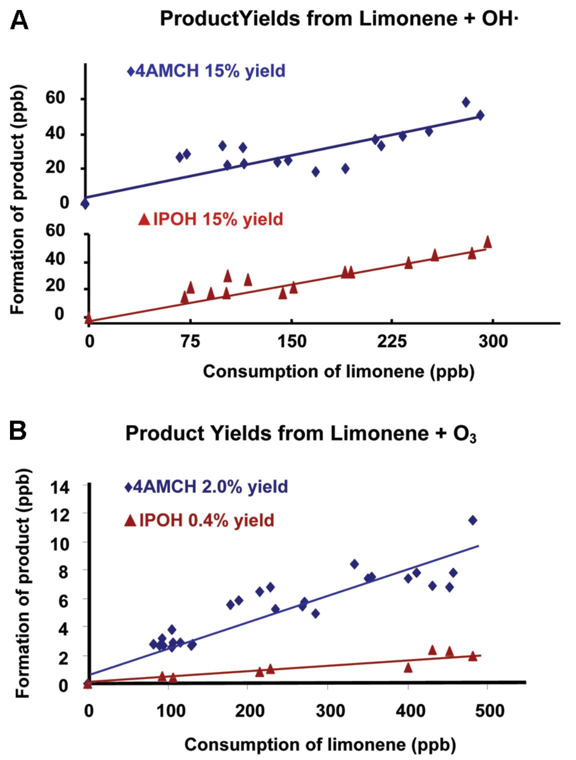


FIGURE 1. Plots of products formed versus limonene reacted. Product concentrations are reactant corrected using eq 1. (A) Yields of 4-acetyl-1-methylcyclohexene (4AMCH ♦) and 3-isopropenyl-6-oxoheptanal (IPOH ▲) from limonene + OH· reaction. (B) Yields of 4AMCH ♦ and IPOH ▲from limonene + O$_3$ reaction.

Products and their yields from the limonene + OH· reaction include 4-acetyl-1-methylcyclohexene (4AMCH) (15 ± 3%), dihydrocarvone (2.3 ± 0.4%), 2-(4-methylcyclohex-3-en-1-yl)propanal (2.3 ± 0.4%), glyoxal (0.5 ± 0.1%), 3-oxobutanal (0.4 ± 0.1%), 4-oxopentanal (0.4 ± 0.1%), and 3-isopropenyl-6-oxoheptanal (IPOH) (15 ± 2%). IPOH and 4AMCH were the products found in the greatest abundance. Plots showing these yields may be viewed in Figure 1A. The total percent yield of carbonyl reaction products was 36% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 33%.

Products and their yields from the limonene + O$_3$ reaction include 4AMCH, (2.0 ± 0.2%), 2-hydroperoxy-3,4-dimethylpent-4-enal (2.3 ± 0.3%), glyoxal (0.4 ± 0.04%), and IPOH (0.4 ± 0.1%). Figure 1B is a plot of the yields of 4AMCH and IPOH from the limonene + O$_3$ reaction. The total percent yield of carbonyl reaction products was 5.1% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 3.9%.

Alpha-Terpineol Results. The products observed from the α-terpineol + OH· reactions were consistent with those observed previously (*23*). Yields of these products have not been previously measured. All percent yield and carbon mass balance results may be viewed in Table 2.

Products and their yields from the reaction of α-terpineol + OH· include 6-hydroxyhept-5-en-2-one (20 ± 3%), 4-methyl-3-cyclohexen-1-one (5.7 ± 0.6%), 4-oxopentanal (2.2 ± 0.6%), glyoxal (1.4 ± 0.3%), and methylglyoxal (0.5 ± 0.1%). Acetone was also observed as a product from the α-terpineol + OH· reaction; however, due to chromatographic interference with PFBHA, its yield could not be measured. A plot of the yield of 6-hydroxyhept-5-en-2-one may be viewed in the Supporting Information. The total percent yield of carbonyl reaction products was 30% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 20%.

Products and their yields from the reaction of α-terpineol + O$_3$ reaction include 6-hydroxyhept-5-en-2-one (31 ± 3%), methylglyoxal (1.9 ± 0.2%), and 4-oxopentanal (0.6 ± 0.3%). A plot of the yield of 6-hydroxyhept-5-en-2-one may be viewed in the Supporting Information. The total percent yield of carbonyl reaction products was 34% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 22%.

Geraniol Results. The products in this study were consistent with previous experimental and modeling studies (*24, 38*). The yields of these products have not been previously measured. All yield data for the geraniol reactions are included in Table 3, and possible formation pathways are described below.

Products and their yields observed from the geraniol + OH· reaction include glycolaldehyde (29 ± 2%), 6-methylhept-5-en-2-one (7.5 ± 1%), glyoxal (0.5 ± 0.1%), and 4-oxopentanal (37 ± 2%). Plots of yields for 4-oxopentanal, glycolaldehyde, and 6-methylhept-5-en-2-one may be viewed in the Supporting Information. The total percent yield of carbonyl reaction products is 74% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 31%.

Products and their yields from the geraniol + O$_3$ reaction include glycolaldehyde (31 ± 4%), 6-methylhept-5-en-2-one (14 ± 2%), 6-hydroxy-4-methyl-4-hexenal (26 ± 5%), glyoxal (0.6 ± 0.1%), methylglyoxal (6.5 ± 0.8%), 4-oxopentanal (3.5 ± 0.6%), and 5-oxopent-4-enal (10 ± 2%). Plots of the yields of glycolaldehyde, 6-methylhept-5-en-2-one, and methylglyoxal may be viewed in the Supporting Information. The total percent yield of carbonyl reaction products is 92% while the concentrations of the identified compounds corresponded to a carbon mass balance for the reaction of 44%.

Discussion

Limonene. Using the PFBHA derivatization technique several reaction products that were unique to this limonene + OH· reaction study were positively identified through syntheses of oximes, including carvone, dihydrocarvone, and 4-oxopentanal. Mass spectral data of these confirmations may be viewed in the Supporting Information. While a dihydrocarvone formation mechanism is not obvious based on current VOC reaction mechanisms, its formation could be the result of O(^{3}P) (possibly formed from NO$_2$ photolysis) reaction with limonene (*39*). Unfortunately, due to chromatographic interference between the carvone peak and one peak of 2-(4-methylcyclohex-3-en-1-yl)propanal, the carvone yield could not be accurately determined; however, a reasonable yield estimate is 1−2%. Also unique to this study was the proposed reaction product 2-(4-methylcyclohex-3-en-1-yl)propanal which was based upon the observed and chromatographic EI and CI data.

Yields of 4AMCH from the limonene + OH· reaction have been measured previously (*16, 40*). In 1994 Hakola et al. measured the gas-phase concentration of 4AMCH at 20 ± 3% from an initial limonene concentration of 0.3−1.0 ppm (*16*). Larsen et al. measured a 4AMCH yield of 39 ± 15% from an initial limonene concentration of 1.0−2.0 ppm (*40*) in 2001. In this study the yield of 4AMCH was 15 ± 2% from an initial limonene concentration of 0.6−1.0 ppm. With the incorporation of error, this value more closely agrees with that measured by Hakola. In the same 1994 study by Hakola et al., the yield for IPOH was measured to be 29 ± 6% (*16*). The measured IPOH yield here of 15 ± 0.9% is lower than that observed by Hakola.

Yields of 4AMCH from the limonene + O$_3$ reaction have been measured previously in studies using an excess of limonene to O$_3$. Clausen et al. measured a 3−4% yield in

2001 from an initial limonene concentration of 38−45 ppm (*18*), Rupert et al. measured ~1% in 1999 (*17*), and Grosjean et al. measured 2% in 1993 from an initial limonene concentration of 1 ppm (*14*). The 2.0% yield of 4AMCH measured in this study is in good agreement with these previous studies. Additionally, Hakola et al. reported an upper limit of ~4% for 4AMCH (*16*). IPOH is also a reaction product of the limonene + O_3 reaction. A gas-phase IPOH yield of 2−4% was measured by Clausen et al. (*18*), and a yield of ~1% was measured by Rupert et al. (*17*). The yield of IPOH measured in this study was 0.4% and is lower than those measured in previous gas-phase studies.

Unique to this limonene + O_3 investigation was the proposed reaction product 2-hydroperoxy-3,4-dimethylpent-4-enal which was based upon the observed EI and CI chromatographic data. Hewitt and Kok investigated peroxides and hydroperoxides formed from reactions of terpenes with O_3 and determined that hydroperoxides account for a significant percentage of the carbon mass balance. However, they concluded that reactions of cyclic alkenes produce only hydrogen peroxide (H_2O_2) (*19*). Donahue et al. recently proposed a mechanism producing a hydroperoxide via endocyclic oxidation of 4AMCH (*41*). The hydroperoxide proposed in this study is structurally similar and could be formed via a mechanism similar to that proposed by Donahue.

Gas-phase yields of IPOH in this investigation were lower in both limonene + OH• and limonene + O_3 reactions than in previous studies. Investigations of limonene by Larsen et al. with OH• and Glasius et al. with O_3 found IPOH in the particulate phase. If IPOH partitioned to the particulate phase in this study it may not have dissolved in the methanol in the impinger and this could account for the lower yields here. Another IPOH loss mechanism could be loss to the chamber walls. Also, 4-oxopentanal was used as a calibration surrogate for IPOH because both compounds were dicarbonyl structures; however, this may not have been an ideal choice due to the differences in their molecular weights.

α-Terpineol. OH• may react with α-terpineol by either addition to the carbon−carbon double bond in the ring or by hydrogen abstraction. Products formed by OH• addition include 6-hydroxyhept-5-en-2-one, methylglyoxal, and 4-oxopentanal. The product assigned to be 6-hydroxyhept-5-en-2-one has been consistently observed in previous as well as the current experiments (*23*). It is possible that $CH_3C(O)CH_2CH_2CH(C(CH_3)_2OH)CH_2CHO$ decomposes by losing a methyl group and CH_2CHO (which can form glyoxal). The path to its formation may not be clear based on current accepted VOC reaction mechanisms, but based on the mass spectral data (derivatization, chemical ionization, and electron impact ionization) this is the most plausible product. Methylglyoxal and 4-oxopentanal are most likely secondary reaction products. One expected reaction product from OH addition is 3-(1-hydroxy-1-methyl-ethyl)-6-oxo-heptanal, however, this product was not observed in this study or in a previous investigation (*23*). It is possible that the product may be formed and then rapidly dissociate into smaller secondary products such as methylglyoxal and 4-oxopentanal. 4-Methyl-3-cyclohexen-1-one is the main product formed by hydrogen abstraction of the unsaturated tertiary carbon on the ring in Structure 2.

Geraniol. Addition to one of the carbon−carbon double bonds is the main mechanistic path for both OH• and O_3 reactions with geraniol. The two main reactive sites in the geraniol molecule for addition are Sites I and II in Structure 3. Depending on which site addition first takes place, the resulting first generation products are predicted to be either 6-hydroxy-4-methyl-4-hexenal and acetone from Site I, or 6-methylhept-5-en-2-one and glycolaldehyde from Site II. Both 6-hydroxy-4-methyl-4-hexenal and 6-methylhept-5-en-2-one contain a carbon−carbon double bond. If OH• or O_3 are still present, additional reactions may take place between these products and OH• or O_3 to form second generation products including 4-oxopentanal and additional acetone and glycolaldehyde.

One of the predicted reaction products, 6-hydroxy-4-methyl-4-hexenal, was not observed from geraniol + OH• in this study or in a previous study (*24*). It is possible that the product could be formed and reacted rapidly with OH•; however, a comparison of the measured geraniol + OH• rate constant (*24*) of 231×10^{-12} cm^3 $molecule^{-1}$ s^{-1} with an estimated 6-hydroxy-4-methyl-4-hexenal + OH• of 116×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (*37*), suggests that competition for the OH• between geraniol and the reaction product is unlikely under these experimental conditions and further implies that OH• preferentially adds to Site II in Structure 3.

Hazard Assessment. Based on the products observed in the reaction studies and their yields, it may now be possible to begin to transform these data into potential health effects. The Chemical Asthma Hazard Assessment Program developed by Jarvis et al. (*2*) was used to calculate a Hazard Index of the observed oxygenated organic reaction products. The Hazard Index is a value between 0 and 1 determined by comparing the substructures of the chemical of interest against a database of substructures present in known occupational respiratory sensitizers. While the program results should not be used definitively, the closer the Hazard Index is to 1 the stronger the prediction is that the submitted compound has the potential to be a respiratory sensitizer. Both the parent compounds and their oxygenated organic products were evaluated using this tool and the results are presented in Tables 1, 2, and 3. The majority of the products have a higher hazard index than the parent which indicates that the products could possibly have a more adverse role in terms of health effects than the parent compound.

To assess the overall reaction, a weighted Hazard Index was calculated for each parent/reactant scheme using the product percent yields and the Hazard Indices of the products. The total Hazard Index is weighted by the percent yield of each of the products measured in this study. The Hazard Index of limonene is 0.18, and is lower than the weighted Hazard Index of 0.52 for its OH• reaction products and the weighted index of 0.37 for its O_3 reaction products. The Hazard Index of α-terpineol is 0.15 and is similar to the product weighted Hazard Index of 0.19 for its OH• reaction products, and 0.15 for its O_3 reaction products. The Hazard Index of geraniol is 0.15 and was lower than the weighted Hazard Index of 0.34 for its OH• reaction products, and 0.33 for its O_3 reaction products.

The low values of the correction factors for the yields suggest that the products may linger in the gas phase, depending on air exchange, and possibly accumulate on surfaces to be re-emitted over time. This could lead to increased occupant exposure to products which, as shown by the hazard assessment values, may cause respiratory problems.

Other methods have been proposed to identify which chemical exposures lead to sensory irritation. For example, Kuwabara et al. recently assessed the applicability of using chemical RD_{50} values to determine human health risk assessment (*42*). The correlation between the RD_{50} and Lowest Observable Acute Effect Level (LOAEL) values for specific chemicals suggests the ability to determine chemical-induced sensory irritation by using RD_{50} values (*42*).

With the exception of the limonene + O_3 reaction, the carbon mass balances ranged from approximately 20 to 40% in this investigation of fragrance compounds. Many of the same products were observed from reactions with each fragrance compound. Often those products found with the highest percent yields were small, containing only 2 or 3 carbon atoms, and only contributed a fraction to the total carbon mass balance. As an example, percent yields of glycolaldehyde in both the OH• and O_3 reactions with geraniol were approximately 30%, however because glycolaldehyde contains only 2 carbon atoms, it only contributed approximately 6% to the carbon mass balance of each reaction.

Recent studies show that particulate matter is formed from reactions of limonene + O_3 (*43*) and gas-phase partitioning of products into the particulate phase (*13, 40*). The low total percent yield from the reaction of limonene with O_3 suggests that many of the reaction products were not captured using the PFBHA derivatization technique because of either the structure of the reaction product or possibly due to partitioning to the particulate phase or loss to the chamber walls. This could also be a source of undetected carbon in the α-terpineol and geraniol reactions.

From the data in this study we are able to conclude that by using PFBHA derivatization in combination with mass spectrometry it is possible to quantify yields of some of the oxygenated organic products in possible indoor reactions. The carbon mass balance indicates that a large percentage of carbon is not detected. Other compounds that may be formed but not detected with the PFBHA technique include carboxylic acids, hydroperoxides, hemiacetals, hemiketals, and secondary ozonides (*44, 45*). Although the technique has been used successfully to detect carboxylic acid compounds in previous studies (*22*) including limonene studies by Glausius et al. (*13*) and Clausen et al. (*18*), none were detected in any of the reaction schemes in this investigation. When product yield data from several previous studies of limonene + O_3 were combined, a carbon mass balance of 17−19% was calculated (*13, 17, 18*). Clearly many of the reaction products remain undetected using various techniques. New analytical methods should be developed for a better understanding of these reaction mechanisms and to better identify and quantify additional oxygenated organic products that may be produced in gas-phase reactions in the indoor environment that current techniques do not capture.

Acknowledgments

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.

Supporting Information Available

Additional yield plots, correction factors, and mass spectral confirmations of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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