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Gas-Phase Chemistry of α-Terpineol with Ozone and OH Radical: Rate Constants and Products

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A bimolecular rate constant, $k_{\mathrm{OH}+\alpha\text{-terpineol}}$, of (1.9 ± 0.5) × 10^{-10} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ was measured using gas chromatography/mass spectrometry and the relative rate technique for the reaction of the hydroxyl radical (OH) with α-terpineol (1-methyl-4-isopropyl-1-cyclohexen-8-ol) at (297 ± 3) K and 1 atm total pressure. Additionally, a bimolecular rate constant, $k_{\mathrm{O_3}+\alpha\text{-terpineol}}$, of (3.0 ± 0.2) × 10^{-16} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ was measured by monitoring the first order decrease in ozone concentration as a function of excess α-terpineol. To better understand α-terpineol's gas-phase transformation in the indoor environment, the products of the α-terpineol + OH and α-terpineol + O_3 reactions were also investigated. The positively identified α-terpineol/OH reaction products were acetone, ethanedial (glyoxal, HC(=O)C(=O)H), and 2-oxopropanal (methyl glyoxal, $CH_3C(=O)C(=O)H$). The positively identified α-terpineol/O_3 reaction product was 2-oxopropanal (methyl glyoxal, $CH_3C(=O)C(=O)H$). The use of derivatizing agents *O*-(2,3,4,5,6-pentalfluorobenzyl)hydroxylamine (PFBHA) and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) clearly indicated that several other reaction products were formed. The elucidation of these other reaction products was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible α-terpineol/OH and α-terpineol/O_3 reaction mechanisms based on previously published volatile organic compound/OH and volatile organic compound/O_3 gas-phase reaction mechanisms.

Introduction

In the United States, it is estimated that over 30 million of the total 89 million workers in indoor environments are affected by the work environment in the form of eye, nose, and throat irritations; headache; and fatigue. These health complaints have an estimated impact on worker productivity of tens of billions of dollars annually (*1*, *2*). Unfortunately, there is currently no direct correlation between these complaints and a specific pollutant. In fact, exposures to multiple pollutants in the indoor environment may be responsible (*3*−*9*). There is growing interest in understanding the role volatile organic compound (VOC) gas-phase reaction products have on human health (*10*−*12*).

A recent review of indoor environment chemistry by Weschler highlights several research areas important to the field (*13*). Significant observations from this review paper are that there are still several fundamental unanswered questions regarding the gas-phase chemistry of indoor environments and that the indoor environment is chemically more complex than previously thought. Experimental evidence has implicated that several initiator species such as ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3) are likely to be present indoors and that the VOC concentrations indoors are higher by a factor of 10 or more than typically found in outdoor environments (*13*, *14*).

Oxygenated organic compounds, such as ethers, alcohols, and esters, are becoming more prevalent in the environment as they are substituted for other chemicals in consumer products. While several hydroxyl radical (OH) + oxygenated organic and ozone (O_3) + oxygenated organic bimolecular rate constants are well-known, details pertaining to these reaction mechanisms are limited (*15*, *16*). A few recent studies of the products from OH + oxygenated organic reactions have illustrated the complexity of their gas-phase reaction mechanisms (*17*−*24*). These investigations are needed to support hydroxyl radical and ozone reaction mechanism patterns based on chemical structure−reactivity relationships (*25*).

1-Methyl-4-isopropyl-1-cyclohexen-8-ol (α-terpineol, Figure 1) is a volatile organic alcohol that is a significant component of indoor cleaner emissions and a component of pine oil (*26*). α-Terpineol is also an emission from some molds found in the indoor environment (*27*−*29*).

In the work presented here, the rate constant of the OH radical with α-terpineol was measured by the relative rate method (*30*), while the reaction rate constant of ozone with α-terpineol was measured by monitoring the first order decrease in ozone concentration as a function of excess α-terpineol. The products of the OH + α-terpineol and O_3 + α-terpineol reactions are also reported. Neither the OH rate constant, O_3 rate constant, nor the respective reaction products for α-terpineol have been reported previously.

Experimental Procedures

Apparatus. Experiments to measure the gas-phase rate constant of the OH + 1-methyl-4-isopropyl-1-cyclohexen-8-ol (α-terpineol, Figure 1) reaction were conducted with a previously described apparatus (*21*, *30*−*32*). A brief description is provided here. Reactants were introduced, and samples were withdrawn through a 6.4 mm Swagelok (Solon, OH) fitting attached to a 60−100 L Teflon film chamber. Dry compressed air was added as a diluent to the reaction chambers and measured with a 0−100 L $\mathrm{min^{-1}}$ mass flow controller (MKS, Andover, MA). The filler system was equipped with a syringe injection port facilitating the introduction of both liquid and gaseous reactants into the chambers by a flowing airstream. All reactant mixtures and calibration standards were generated by this system. Irradiations were carried out in a light-tight chamber using 5 mL FEP Teflon-film bags (60−100 L), which were surrounded by the following mix of lamps: six Philips TL40W/03; one GE F40BL; two QPANEL (Cleveland, OH) UV351; and seven QPANEL UV340. This lamp mixture approximates solar radiation from 300 to 450 nm.

All reaction kinetic samples were quantitatively monitored using an Agilent (Palo Alto, CA) 6890 gas chromatograph with a 5973 mass selective detector (GC/MS) and Agilent series Chem Station software. Gas samples were cryogenically collected employing an Entech (Simi Valley, CA) 7100 sampling system utilizing the following trap and temperature parameters: 50 mL of chamber contents was collected onto

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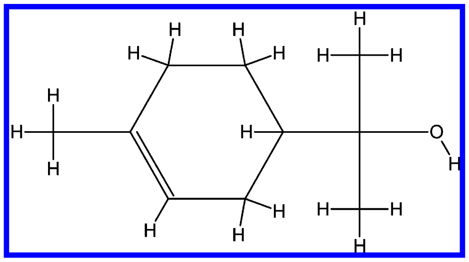


FIGURE 1. 1-Methyl-4-isopropyl-1-cyclohexen-8-ol α-terpineol.

trap 1 (packed with Tenax TA) at −150 °C. After sample collection, trap 1 was heated to 40 °C, and the sample was transferred under a flow of ultrahigh purity helium (UHP He) onto trap 2 (packed with Tenax TA) cooled to −30 °C. Trap 2 was then heated to 180 °C, and the sample was transferred under a UHP He flow onto trap 3, a silanized 0.53 mm i.d. tube cooled to −160 °C, which was subsequently heated to 220 °C to inject the sample onto the GC column (Restek (Bellefonte, PA) Rtx VRX (0.25 mm i.d., 30 m long, 1.4 μm film thickness)). These series of cryogenic trap manipulations reduced the background water level, ensured consistency of replicate samples, and improved the chromatograph peak shapes. The GC temperature program used was initial temperature of 45 °C held for 8 min after sample injection, then increased 10 °C/min to 220 °C and held for 4 min. The Agilent 5973 mass selective detector was tuned using perfluorotributylamine (FC-43). Full scan electron impact ionization spectra were collected from m/z 35 to 220. Preliminary compound identifications from the Agilent 6890/5973 GC/MS data sets were made by searching the NIST 98 Mass Spectral Library.

Experiments to measure the reaction of ozone with 1-methyl-4-isopropyl-1-cyclohexen-8-ol were conducted using a similar chamber as described previously, but the ozone concentration was measured using a UV photometric ozone analyzer (Thermo Environmental model 49-C Franklin, MA). An additional port was added to the Teflon chamber to facilitate the injection of ozone.

Reaction product identification experiments were performed utilizing direct sampling and chemical derivatization methods. Direct gas-phase sampling and Agilent 6890/5973 GC/MS analysis of the reaction chamber contents was performed as described above. Collection and derivatization of the gas-phase aldehyde and ketone reaction products used *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA), while derivatization of alcohol and carboxylic acid reaction products utilized PFBHA with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Derviatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system (*33*). The combination of PFBHA/BSTFA derivatizations was used previously to identify the reaction products and propose reaction mechanisms for the ozonolysis of α-pinene and Δ^3-carene (*33*, *34*). Experimental methods for reaction product identification were similar to methods used for kinetic experiments except that the reference compound was excluded from the reaction mixture.

The derivatized aldehydes, ketones, and alcohols were analyzed with a Varian 3800 gas chromatograph and a Varian Saturn 2000 ion trap mass spectrometer operated in the EI mode. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm i.d., 30 m long, 1 μm film thickness)) column and the following GC oven parameters: 60 °C for 1 min, then 10 °C/min to 280 °C and held for 10 min. 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 180 °C/min to 250 °C and held to the end of the chromatographic run (*33*). The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full scan electron impact ionization spectra were collected from m/z 40 to 650.

OH radicals, one of the primary oxidizing radicals in the indoor environment (*11*, *35*−*37*), were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air (*30*).

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{1}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{2}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{3}$$

CH_3ONO was prepared in gram quantities using the method of Taylor et al. (*38*) and stored in a lecture bottle at room temperature. The CH_3ONO purity (>95%) was verified by GC/MS.

Ozone (O_3) was produced by photolyzing air with a mercury pen lamp in a separate Teflon bag. Aliquots of this O_3/air mixture were added to the Teflon reaction chamber using a gastight syringe.

Reagents. All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): hexane (99%), 2,5-dimethylfuran (99%), isoprene (99%), α-terpineol (90% solution), 4-methylcyclohexanone (99%), 3-methyl-2-cyclohexen-1-one (98%), 6-methyl-5-hepten-2-one (99%), acetonitrile (99.93%), *N*,*O*-bis-(trimethyl silyl) trifluoroacetamide (BSTFA) (99+ %), *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) (98+ %); from ULTRA Scientific (North Kingstown, RI): 2-methyl propanal (98%); from Fisher Scientific (Pittsburgh, PA): methanol (99%); from Spectrum Analytical (New Brunswick, NJ): methylene chloride (99.5%). Water was distilled, deionized to a resistivity of 18 MΩ cm, and filtered using a Milli-Q filter system (Billerica, MA). 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.

The experimental procedures for determining the α-terpineol + OH reaction kinetics were similar to those described previously (*22*, *23*).

$$\alpha\text{-terpineol} + OH \xrightarrow{k_{OH+\alpha\text{-terpineol}}} \text{products} \tag{4}$$

$$\text{reference} + OH \xrightarrow{k_R} \text{products} \tag{5}$$

The rate equations for reactions 4 and 5 are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\alpha\text{-terpineol}]_0}{[\alpha\text{-terpineol}]_t}\right) = \frac{k_{OH+\alpha\text{-terpineol}}}{k_R}\ln\left(\frac{[R]_0}{[R]_t}\right) \tag{6}$$

If a reaction with OH is the only removal mechanism for α-terpineol and a reference, a plot of $\ln([\alpha\text{-terpineol}]_0/[\alpha\text{-terpineol}]_t)$ versus $\ln([R]_0/[R]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_R yields $k_{OH+\alpha\text{-terpineol}}$ (Figure 2). The OH rate constant experiments for α-terpineol employed the use of two reference compounds, 2,5-dimethyl furan and isoprene. The use of two different reference compounds with different OH rate constants more definitively assured the accuracy of the α-terpineol/OH rate constant and demonstrates that other reactions do not remove α-terpineol.

For the α-terpineol/OH kinetic experiments, the typical concentrations of the pertinent species in the 60−100 L Teflon chamber were 0.3−0.6 ppm (0.7−1.4 × 10^{13} molecule cm^{-3})

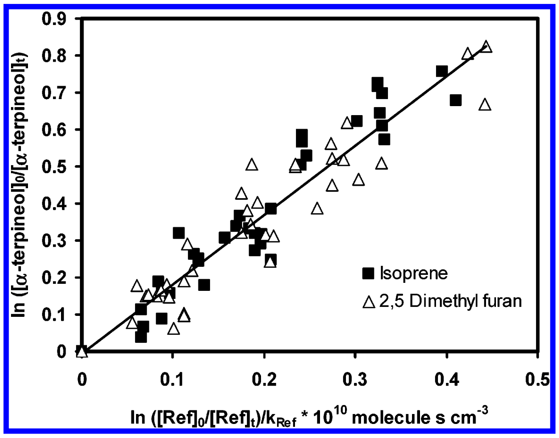


FIGURE 2. 1-Methyl-4-isopropyl-1-cyclohexen-8-ol relative rate plot with 2,5-dimethyl furan (△) and isoprene (■) as reference compounds. The OH + α-terpineol rate constant, $k_{\alpha\text{-terpineol+OH}}$, measured is (1.87 ± 0.13) × 10^{-10} cm^3 molecule^{-1} s^{-1}.

α-terpineol, 0.5−0.7 ppm (1.2−1.6 × 10^{13} molecule cm^{-3}) reference, 10 ppm (23 × 10^{13} molecule cm^{-3}) CH_3ONO, and 0−0.6 ppm (0−1.4 × 10^{13} molecule cm^{-3}) NO in air. α-Terpineol was diluted in methanol to 45 and 18% (volume %) solutions. This facilitated the transfer of α-terpineol to the gas phase since it is a solid at room temperature. Methanol was chosen because both the methanol/OH and the methanol/O_3 rate constants and reaction products were not expected to affect the reaction system. These mixtures were allowed to reach equilibrium before initial species concentration ($[X]_0$) samples were collected. Typically, four photolysis intervals of 2−5 s each were used on the reaction mixture for a combined total photolysis time of approximately 8−40 s. The total ion chromatogram (TIC) from the Agilent 5973 mass selective detector was used to determine α-terpineol and reference concentrations.

The experimental methods and parameters for observation of α-terpineol/OH reaction products were similar to those for reaction rate experiments except that the reference compound was excluded from the reaction mixture. The reaction mixtures were irradiated for 2−10 s intervals followed by sample collection. Commercially available samples of the identified products were analyzed to verify matching ion spectra and chromatographic retention times.

The experimental procedures for determining the α-terpineol + O_3 reaction kinetics were similar to those described previously (*39*).

$$\alpha\text{-terpineol} + O_3 \xrightarrow{k_{O_3+\alpha\text{-terpineol}}} \text{products} \qquad (7)$$

The α-terpineol/ozone reaction was determined using an excess of α-terpineol relative to ozone. During the reaction, the ozone concentration decreased in a first order fashion. Ozone loss was measured over time as a function of α-terpineol concentration. The range of α-terpineol concentrations was 0.3−1.2 ppm (0.7−2.9 × 10^{13} molecule cm^{-3}), while the ozone concentration was initially 0.1 ppm (0.2 × 10^{13} molecule cm^{-3}). Ozone was injected into the reaction chamber as it was being filled with air and α-terpineol. After filling, the chamber was connected within 20 s to the Thermo Electron UV photometric ozone analyzer Model 49C, and ozone concentration measurements integrated over 10 s time intervals were collected up to a total of 1100 s. The rate of ozone loss (k') as a function of α-terpineol concentration is shown in Figure 3. The negligible loss of ozone to the chamber walls and/or reaction with methanol was verified by injecting the same volumes of ozone and methanol in air only and monitoring the ozone concentration as described previously.

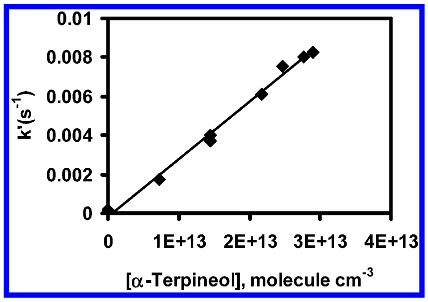


FIGURE 3. Plot of ozone loss rate vs α-terpineol concentration. Pseudo first-order rate constant of α-terpineol + ozone reaction is (3.0 ± 0.2) × 10^{-16} cm^3 molecule^{-1} s^{-1}.

Derivatization of the aldehyde and ketone reaction products was initiated by the flowing of 15−25 L of chamber contents at 3.8 L min^{-1} through 3 mL of acetonitrile in an impinger with no effort to prevent acetonitrile evaporation during sample collection. The sample was removed from the impinger, and 200 μL of 0.02 M PFBHA was added to derivatize aldehyde and ketone reaction products to oximes (*33*) over a 24−48 h time period in the dark. The reacted solutions were gently blown to dryness with UHP N_2 and reconstituted with 100 μL of methanol, and 1 μL of the reconstituted solution was injected onto the Varian 3800/Saturn 2000 GC/MS system. The derivatization of hydroxy groups (either alcohol or carboxylic acid) was achieved by subsequent addition of 20 or 100 μL of commercially available BSTFA to the PFBHA oximes reconstituted with 100 μL of hexane/methylene chloride (1:1). 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 (*33*).

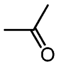
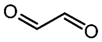
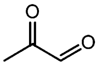
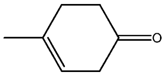
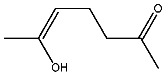
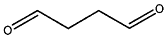
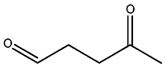
Chemical ionization mass spectra using acetonitrile were also collected on the dervatized reaction products allowing the determination of the PFBHA or PFBHA/BSTFA derivatized compound's molecular weight.

To determine possible chromatographic interferences from reference/OH reaction products, both α-terpineol and reference compounds were reacted with the OH radical in separate experiments and analyzed as described previously. No chromatographic interferences were observed. Two experiments were conducted to determine the stability of the reference and α-terpineol coexisting in the same bag. First the reference and α-terpineol were injected into the bag, analyzed, photolyzed for 6 min, and reanalyzed. In a separate experiment, methyl nitrite, NO, reference, and α-terpineol were injected into the bag, analyzed, left for several hours, and then reanalyzed. None of these preliminary experiments yielded chromatographic peak interferences or observable reactions occurring without photoinitiation. At the end of each run, the Teflon bag was cleaned by flushing the bag 6 times with air (<0.1 ppm total hydrocarbon). Measurements of an air filled bag showed no cross contamination between runs. All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 2.5% was achieved with the described sampling method utilizing the Entech 7100/Agilent 6890/5973 cryogenic sampling GC/MS system.

Results

Hydroxyl Radical/α-Terpineol Reaction Rate Constant. The OH rate constant for 1-methyl-4-isopropyl-1-cyclohexen-8-ol (α-terpineol, Figure 1) was obtained using the relative rate method described previously. Typically, five experimental runs were conducted on each α-terpineol/reference pair. The plot of a modified version of eq 6 is shown in Figure 2. The $\ln([R]_0/[R]_t)$ term is divided by the respective reference

TABLE 1. Molecular Structure and Confirmation Methods of Some α-Terpineol/OH and α-Terpineol/O$_3$ Reaction Products Based on Data from PFBHA Derivatizations

α-terpineol/OH or α-terpineol/O$_3$ reaction product name	molecular structure	molecular weight (amu)	derivatized molecular weight (amu)	observed ions of PFBHA derivatized reaction product (relative intensity %)	confirmation method
acetone (OH reaction only)		58	253		oxime derivatization and direct gas-phase detection
ethanedial (glyoxal)		58	448		oxime derivatization
2-oxopropanal (methyl glyoxal)		72	462		oxime derivatization
4-methyl-3-cyclohexen-1-one		110	305	79(100), 107(75), 181(70), 277(15), 289(10)	
6-hydroxy-hept-5-en-2-one		128	323	43(70), 79(40), 107(40), 142(15), 181(100), 288(60), 305(90)	
1,4-butanedial		86	476	43(25), 181(100), 250(20), 279(15)	
4-oxopentanal		100	490	181(100), 207(50), 250(70)	

rate constant (isoprene (1.01 ± 0.25) × 10^{-10}cm^3 molecule^{-1} s^{-1} and 2,5-dimethyl furan (1.32 ± 0.33) × 10^{-10} cm^3 molecule^{-1} s^{-1}) (*15, 16, 23, 40*) and multiplied by 10^{10} cm^{-3} molecule s resulting in a unitless number. This yields a slope that is equal to the hydroxyl radical/α-terpineol rate constant, $k_{OH+\alpha\text{-terpineol}}$, divided by 10^{-10} cm^3 molecule^{-1} s^{-1}. This modification allows for a direct comparison of the two reference compound/α-terpineol data sets. The slope of the line shown in Figure 2 yields a hydroxyl radical bimolecular rate constant, $k_{OH+\alpha\text{-terpineol}}$, of (1.87 ± 0.13) × 10^{-10} cm^3 molecule^{-1} s^{-1}. The data points at the origin are experimental points because preirradiation, t = 0, data showed no detectable loss of α-terpineol or reference. The error in the rate constant stated previously is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants (±25% for isoprene and 2,5-dimethylfuran) used to derive the α-terpineol/OH rate constant yields a final value for $k_{OH+\alpha\text{-terpineol}}$ of (1.9 ± 0.5) × 10^{-10} cm^3 molecule^{-1} s^{-1} (*15, 16, 40*).

The α-terpineol/OH rate constant, $k_{OH+\alpha\text{-terpineol}}$, has not been previously reported. The observed rate constant can be compared with a $k(\text{cal})_{OH+\alpha\text{-terpineol}} = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, calculated using a structure reactivity relationship (*25*).

Ozone/α-Terpineol Reaction Rate Constant. The O$_3$ rate constant for 1-methyl-4-isopropyl-1-cyclohexen-8-ol (α-terpineol, Figure 1) was obtained by monitoring the ozone concentration decay in excess α-terpineol. The ozone concentration decreased in a first-order fashion. The plot of the ozone loss rate (k') as a function of α-terpineol concentration is shown in Figure 3. The slope of the line shown in Figure 3 yields an ozone bimolecular rate constant, $k_{O^3+\alpha\text{-terpineol}}$, of (3.0 ± 0.2) × 10^{-16} cm^3 molecule^{-1} s^{-1}. The error in the rate constant stated previously is the 95% confidence level from the random uncertainty in the slope. The α-terpineol/O$_3$ rate constant, $k_{O_3+\alpha\text{-terpineol}}$, has not been previously reported. The observed rate constant can be compared with a $k(\text{cal})_{O_3+\alpha\text{-terpineol}} = 4.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, calculated using a structure reactivity relationship (*25*).

α-Terpineol/OH Reaction Products. The reaction products observed from the initial α-terpineol/OH hydrogen abstraction or OH addition to the carbon−carbon double bond are consistent with previously observed hydroxyl radical reaction mechanisms for oxygenated organic species (*17–24*). Typically, the parent oxygenated organic compound reacts with OH to subsequently generate other oxygenated organic products. For α-terpineol, the α-terpineol/OH reaction products observed and positively identified, using the pure compound for verification either by direct gas-phase detection or derivatization or both, were acetone, 2-oxopropanal (methyl glyoxal, CH$_3$C(=O)C(=O)H), and ethanedial (glyoxal, HC(=O)C(=O)H) and are listed in Table 1. Many other α-terpineol/OH reaction products were observed utilizing the derivatization methods described previously. Elucidation of these other reaction products was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible α-terpineol/OH reaction mechanisms based on previously published volatile organic compound/OH gas-phase reaction mechanisms (*15, 17–24*). These other reaction products are also listed in Table 1. The results for both the positively identified reaction products and the other observed reaction products are described next.

Derivatization of nonsymmetric carbonyls using PFBHA or PFBHA/BSTFA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak 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 (typically >40%) and a [PFBHA oxime + 181]$^+$ ion (due to reactions in the ion trap mass spectrometer) (*33*). In most cases, the m/z 181 ion relative intensity for the chromatographic peaks due to α-terpineol/OH and 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 (*33*). The mass spectra of compounds that were additionally derivatized with BSTFA had m/z 73 ions from the $[Si(CH_3)_3]^+$ fragments (*33*).

The following chronological chromatographic retention time results and mass spectra data were observed utilizing PFBHA or PFBHA/BSTFA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The reaction products reported here had chromatographic peak areas proportional to initial α-terpineol concentrations and were observed only after OH initiation of α-terpineol/methanol/methyl nitrite/NO/air mixtures or addition of O_3 to α-terpineol/methanol/air. Derivatization experiments performed in the absence of α-terpineol but in the presence of all other chemicals in the reaction chamber (methanol/methyl nitrite/NO/air) did not result in any of the data reported next except for small amounts (as noted by chromatographic peak areas) of acetone, 2-oxopropanal, and ethandial. Acetone was also observed in prephotoinitiated α-terpineol/OH or pre-ozonated α-terpineol/O_3 derivatization samples. However, the acetone, 2-oxopropanal, and ethandial oxime peak areas increased significantly with α-terpineol/OH reaction initiation, indicating that acetone, 2-oxopropanal, and ethandial are likely products of the α-terpineol + OH reaction. Only 2-oxopropanal peak areas increased significantly with α-terpineol/O_3 reaction initiations indicating that 2-oxopropanal was a likely reaction product. Aside from the positively identified reaction products (Table 1) with the synthesis of the derivatized oxime compounds, α-terpineol/OH and α-terpineol/O_3 reaction product identification was derived from mass spectra data and previously published VOC/OH and VOC/O_3 reaction mechanisms (*17*–*24*, *33*).

Acetone. Acetone was identified using the Agilent 6890/5973 GC/MS system and PFBHA derivatization method described previously. The acetone oxime ($PFBHA{=}C(CH_3)_2$) was observed at retention time of 11.2 min employing the Varian 3800/Saturn 2000 GC/ion trap mass spectrometer system described previously. Acetone oxime was synthesized to confirm this chromatographic assignment. Acetone oxime was observed in prephotolysis samples, but the peak area increased upon initiation of an α-terpineol/OH reaction indicating acetone as a α-terpineol/OH reaction product.

Oxime at Retention Time 17.8 min. The oxime observed with a chromatographic peak at a retention time of 17.8 min had ions of m/z 79, 107, 181, 277, and 289. Using acetonitrile for chemical ionization, an M + 1 ion of m/z 306 was observed. Using the derivatized molecular weight of 305 for the oxime suggests a carbonyl compound with a molecular weight of 110. The single chromatographic peak suggests an aldehyde structure or a symmetric ketone structure. A proposed α-terpineol/OH reaction product assignment of 4-methyl-3-cyclohexen-1-one (see Table 1) was made based upon the observed data. To support this assignment, both 3-methyl-2-cyclohexen-1-one and 4-methylcyclohexanone were derivatized and compared chromatographically to the observed α-terpineol/OH data. The retention time for the 3-methyl-2-cyclohexen-1-one oxime was 18.3 min and had a very similar mass spectrum to the one observed from α-terpineol/OH experiments. The retention time for the 4-methylcyclohexanone oxime was 17.3 min and had a different mass spectrum from the one observed from α-terpineol/OH experiments. A small product peak that increased in size as the α-terpineol/OH reaction progressed was observed using the Entech cryogenic collection/Agilent GC/MS system. A comparison of the mass spectrum of this product peak matches very closely with the published mass spectrum for 4-methyl-3-cyclohexen-1-one by Hakola et al (*41*).

Oxime at Retention Time 19.3 min. The oxime observed with a chromatographic peak at a retention time of 19.3 min was observed as a reaction product of α-terpineol/OH and α-terpineol/O_3 and had ions of m/z 43, 79, 107, 142, 181, 290, and 305. The use of chemical ionization mass spectrometry indicated that this oxime had a molecular mass of 323, suggesting that the reaction product was a carbonyl compound with a molecular weight of 128. To determine if this carbonyl reaction product contained an alcohol group (-OH) as well, a separate experiment using the PFBHA/BSTFA derivatization method described previously yielded a small chromatographic peak with a 20.2 min retention time and a mass spectrum with a large relative intensity m/z 305 ion and additional ions of m/z 73, 75, 181, 207, and 288. Chemical ionization mass spectrometry indicated that this doubly derivatized (PFBHA and BSTFA) reaction product had a molecular mass of 395, suggesting that the reaction product was a carbonyl compound with an alcohol group with a molecular weight of 128. If the large m/z 305 ion observed in the PFBHA derivatized, PFBHA/BSTFA derivatized, and the PFBHA/BSTFA chemical ionization samples is due to the $[F_5C_6CH_2ON{=}C(CH_3)(CH_2CH_2C{=}C(CH_3))]^+$ fragment, then the m/z data stated previously supports the proposed α-terpineol/OH and α-terpineol/O_3 reaction product assignment of 6-hydroxy-hept-5-en-2-one ($(HO)(H_3C)C{=}CHCH_2CH_2C({=}O)CH_3$).

Ethanedial (Glyoxal, HC(=O)C(=O)H). The chromatographic peaks for the oxime observed at 20.9 and 21.0 min was observed as a reaction product of α-terpineol/OH and had ions at m/z 117, 181, 251, 253, 267 (very low relative intensity), and 448 (relative intensity 25% of the m/z 181 ion). The m/z 448 ion is the result of a double PFBHA derivatization, indicating a reaction product with a molecular weight of 58. The assignment of glyoxal was verified by matching mass spectra and a retention time of a synthesized PFBHA-glyoxal oxime.

2-Oxopropanal (Methyl Glyoxal, $CH_3C({=}O)C({=}O)H$). The single peak for the oxime observed at 21.3 min was observed as a reaction product of α-terpineol/OH and α-terpineol/O_3 and had ions at m/z 117, 181, 265, 432, and 462. The m/z 462 ion is the result of a double PFBHA derivatization, indicating a reaction product with a molecular weight of 72. The PFBHA-methyl glyoxal oxime was synthesized to confirm this chromatographic assignment, and the second chromatographic peak for PFBHA-methyl glyoxal overlaps with the 21.0 min peak of PFBHA-glyoxal.

Oxime at Retention Times 21.6, 22.0, and 22.1 min. The oxime observed with chromatographic peaks at retention times of 21.6, 22.0, and 22.1 min was observed as a reaction product of α-terpineol/OH and had ions of m/z 43, 181, 250, and 279. Using acetonitrile for chemical ionization, an M + 1 ion of m/z 477 was observed. Using the derivatized molecular weight of 476 for the oxime suggests a doubly derivatized ketone with a molecular weight of 86. A proposed α-terpineol/OH reaction product assignment of butanedial ($HC({=}O)CH_2CH_2C({=}O)H$) was made based upon the observed data.

Oxime at Retention Times 21.8 and 22.8 min. The oxime observed with chromatographic peaks at retention times of 21.8 and 22.8 min was observed as a reaction product of α-terpineol/OH and had ions of m/z 70, 181, and 250. Using acetonitrile for chemical ionization, an M + 1 ion of m/z 491 was observed. Using the derivatized molecular weight of 490 for the oxime suggests a doubly derivatized ketone with a molecular weight of 100. A proposed α-terpineol/OH reaction product assignment of 4-oxopentanal ($HC(=O)CH_2CH_2C(=O)CH_3$) was made based upon the observed data.

Discussion

α-Terpineol (Figure 1) is a molecule with eight distinct sites for possible hydrogen abstraction and one site for OH addition (*15*, *16*). The carbon−carbon double bond and the unsaturated tertiary carbon atom on the ring contribute approximately 87% (OH-addition) and 4% (H-abstraction), respectively, to the calculated α-terpineol/OH rate constant of 1×10^{-10} cm^3 molecule^{-1} s^{-1} (*25*). This calculated value is in agreement with the measured value reported here ($(1.9 \pm 0.5) \times 10^{-10}$cm^3 molecule^{-1} s^{-1}), considering that OH rate constants calculated using a structure reactivity are typically within a factor of 2 of the measured OH rate constant (*25*).

Ozone reacts with α-terpineol by addition to the carbon−carbon double bond. The estimated α-terpineol/O_3 rate constant using structure reactivity is 4×10^{-16} cm^3 molecule^{-1} s^{-1} and is consistent with the measured value reported here $(3.0 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (*25*).

The α-terpineol/OH reaction experimental parameters, described next, were set to minimize other side reactions and highlight the first OH hydrogen abstraction and OH addition step. The α-terpineol concentration was kept low enough to prevent aerosol formation, and the photolysis times were as short as necessary to produce sufficient OH concentrations for the α-terpineol/OH reaction but not necessarily for reaction product/OH reactions. Additionally, nitric oxide (NO) was added to facilitate the generation of OH and to minimize ozone (O_3) and nitrate radical (NO_3) formation, preventing other possible radical reactions. The possible mechanistic steps leading to product formation are described next. Depending on the nature of the radicals formed in reactions 4 and 7, some reaction products may be formed by multiple pathways.

Previous investigations of the terpene/OH and terpene/O_3 reactions have been conducted in the interest of understanding the atmospheric impact of biogenic emissions (*33*, *43*, *44*). Terpenes are emitted in large concentration by vegetation (millions of tons per year) and have many potential hydroxyl reactive sites such as hydrogens attached to carbons on bridging rings and carbon−carbon double bonds (*45*). There is scientific interest in nighttime OH radical formation in the atmosphere, and terpene/O_3 reactions are some of the more likely avenues for nighttime OH formation (*33*, *43*, *44*). Additionally, the terpene/O_3 reaction is considered the most significant source for OH formation in indoor environments (*13*).

Previous investigations of the terpene/OH and terpene/O_3 reaction mechanism have identified the most significant reaction step as the addition of the OH radical or ozone into the carbon−carbon double bond yielding an electronically excited species (*33*, *41*, *43*). However, while most investigations of these reactions have identified reaction products such as ketones, aldehydes and carboxylic acids that retain most of the terpene parent molecular structure, it has been observed from α-terpineol that many smaller diketone reaction products have been formed. This indicates that once the ring is opened at the carbon−carbon double bond, it begins to react with oxygen and dissociate into smaller oxygenated products such as 2-oxopropanal, ethanedial, butanedial, 4-oxopentanal, and acetone. There was only one product, proposed to be 6-hydroxy-hept-5-en-2-one, that retained a significant portion of the parent α-terpineol molecule.

Recently, PFBHA-coated solid-phase microextraction (SPME) fibers were used for the passive sampling of the gas-phase reaction products of *Z*-3-hexen-1-ol/OH, 2-methyl-3-buten-2-ol/OH, and a series of diols/OH. These reactions yielded products that supported OH addition to the carbon−carbon double bond and hydrogen abstraction from the C−H bonds of the HC(OH) groups (*41*, *42*). However, if OH was added to the α-terpineol carbon−carbon double bond, one of the expected reaction products would be 3-(1-hydroxy-1-methyl-ethyl-)-6-oxo-heptanal ($H_3CC(=O)CH_2CH_2C(H)(C(OH)(CH_3)_2)CH_2C(=O)H$). Unfortunately, 3-(1-hydroxy-1-methyl-ethyl-)-6-oxo-heptanal was not observed in the experimental system described previously, but if formed, it could adhere to the chamber walls and be removed from the gas phase.

The combination of PFBHA/BSTFA derivatizations was used recently to identify the reaction products and propose reaction mechanisms for the ozonolysis of α-pinene and Δ^3-carene (*33*, *34*). The separate use of PFBHA and PFBHA/BSTFA derivatizations as well as electron impact and chemical ionization mass spectrometry was critical for insight into the possible molecular structures of the α-terpineol/OH and α-terpineol/O_3 reaction products. Comparison of the chromatographic and mass spectroscopic results from the PFBHA and PFBHA/BSTFA methods highlighted the portions of the α-terpineol/OH reaction product molecules that contained alcohol or carboxylic acid groups such as were observed for the proposed reaction product 6-hydroxy-hept-5-en-2-one ($H_3CC(=O)CH_2CH_2C(H)=C(CH_3)(OH)$).

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