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

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Received 1 July 2005; revised 23 November 2005; accepted 7 December 2005

DOI 10.1002/kin.20174 Published online in Wiley InterScience (www.interscience.wiley.com).

> ABSTRACT: A bimolecular rate constant, $k_{OH+dihydromyrcenol}$, of $(38 \pm 9) \times 10^{-12} \text{ cm}^3$ molecule $^{-1}$ s $^{-1}$ was measured using the relative rate technique for the reaction of the hydroxyl radical (OH) with 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol,) at 297 ± 3 K and 1 atm total pressure. Additionally, an upper limit of the bimolecular rate constant, $k_{O_3 + dihydromyrcenol}$, of approximately 2 $\times 10^{-18}$ cm³ molecule⁻¹ s⁻¹ was determined by monitoring the decrease in ozone (O3) concentration in an excess of dihydromyrcenol. To more clearly define part of dihydromyrcenol's indoor environment degradation mechanism, the products of the dihydromyrcenol + OH and dihydromyrcenol + O_3 reactions were also investigated. The positively identified dihydromyrcenol/OH and dihydromyrcenol/O3 reaction products were acetone, 2-methylpropanal (O=CHCH(CH₃)₂), 2-methylbutanal (O=CHCH(CH₃)CH₂CH₃), ethanedial (glyoxal, HC(=O)C(=O)H), 2-oxopropanal (methylglyoxal, CH₃C(=O)C(=O)H). The use of derivatizing agents O-(2,3,4,5,6-pentafluorobenzyl)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 dihydromyrcenol/OH and dihydromyrcenol/O₃ reaction mechanisms based on previously published volatile organic compound/OH and volatile organic compound/O3 gas-phase reaction mechanisms. © 2006 Wiley Periodicals, Inc.* Int J Chem Kinet 38: 451-463, 2006

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INTRODUCTION

Work-related asthma (WRA) has increasingly become one of the most commonly diagnosed respiratory diseases in the United States [1]. The reason for the increases in work-related asthma has been partially

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attributed to the presence of volatile organic compounds (VOCs) [2–5]. VOCs in the indoor environment come from a number of sources, but a significant portion results from the use of cleaning products and air fresheners [6]. These products act not only as primary emission sources for VOCs, but also contribute to the formation of secondary pollutants due to reaction with other indoor constituents [6].

Experimental evidence has implicated that several initiator species such as ozone (O_3) , hydroxyl radical (OH), and nitrate radical (NO_3) are present indoors [7,8]. These indoor reactants can convert VOCs that are present (i.e., cleaning products, air fresheners) into other oxygenated organic compounds such as aldehydes, ketones, and dicarbonyls. In a recent paper by Jarvis et al., chemicals with these carbonyl substructures were associated with the potential to cause work-related asthma [9].

Other oxygenated organic compounds, such as ethers, alcohols, and esters, are also becoming more prevalent in the indoor environment as they are substituted for other chemicals in consumer products. While several hydroxyl radical (OH) + oxygenated organic and ozone (O₃) + oxygenated organic bimolecular rate constants are well known, details pertaining to these reaction mechanisms are limited [10,11]. A few recent studies of the products from OH + oxygenated organic reactions have illustrated the complexity of their gasphase reaction mechanisms [12–20]. These investigations are needed to support OH and O₃ reaction mechanism patterns based on chemical structure–reactivity relationships [21].

Before attributing a particular VOC or group of VOCs to the effect of WRA, identification and quantification of organic compounds present in the indoor environment is necessary to determine occupant exposures. Additionally, the mechanisms from which these are emitted or formed must also be understood to provide a basis for chemical selection based on structure. With this knowledge, new compounds may be synthesized that incorporate environmentally and technically beneficial molecular structures. The information gained from the type of research presented here can lead to more beneficial use of these and similar compounds in the future. One such compound of interest is 2,6dimethyl-7-octen-2-ol (dihydromyrcenol, Structure 1) a volatile organic alcohol that is a significant component of indoor cleaner emissions and a component of the lavender scent [6].

In the work presented here, the rate constant of the OH radical with dihydromyrcenol was measured by the relative rate method. An upper limit for the dihydromyrcenol/O₃ rate constant was also determined by monitoring the decrease in the ozone



Structure 1 2,6-dimethyl-7-octen-2-ol

concentration in an excess of dihydromyrcenol [22]. The products of the OH + dihydromyrcenol and O_3 + dihydromyrcenol reactions are also reported. Neither the OH rate constant, O_3 rate constant, nor the respective reaction mechanisms for dihydromyrcenol have been reported previously.

EXPERIMENTAL METHODS

Apparatus and Materials

Experiments to measure the gas-phase rate constant of the OH+2,6-dimethyl-7-octen-2-ol (dihydromyrcenol, Structure 1) reaction were conducted with a previously described apparatus [16,22-24]. A brief description is provided here. Reactants were introduced, and samples were withdrawn through a 6.4mm Swagelok fitting attached to a 60-100 L Teflon film chamber. Compressed air from the NIOSH facility was passed through anhydrous CaSO₄ (Drierite, Xenia, OH) and molecular sieves (Drierite, Xenia, OH) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers and measured with a $0-100 \text{ Lmin}^{-1}$ mass flow controller (MKS, Andover, MA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed that if contaminants were present they would be below the part per trillion range. 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 air stream. All reactant mixtures and calibration standards were generated by this system. Irradiations were carried out in a light-tight chamber using 5-mil FEP Teflon-film chambers (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 ChemStation 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 were collected onto Trap 1 (packed with Tenax TA) at -150° C. After sample collection, Trap 1 was heated to 40°C and the sample transferred under a flow of ultra high 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 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 an Rtx-VRX (Restek, Bellefonte, PA) GC column (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 (EI) 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 2,6-dimethyl-7-octen-2-ol were conducted using a similar chamber as described above, 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. The gas-phase carbonyl reaction products were derivatized using O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA), while the alcohol and carboxylic acid reaction products were derivatized using PFBHA with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in EI mode [25]. 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 [25,26]. Experimental methods for reaction product identification were similar to methods used for kinetic experiments except the reference compound was excluded from the reaction mixture.

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 [25]. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI spectra were collected from m/z 40 to 650.

OH radicals, one of the primary oxidizing radicals in the indoor environment [27–30], were generated from the photolysis of methyl nitrite (CH₃ONO) in the presence of nitric oxide (NO) in air [22] (Eqs. (1)-(3)).

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
 (1)

 $CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (2)$

$$HO_2 + NO \rightarrow OH + NO_2$$
 (3)

CH₃ONO was prepared in gram quantities using the method of Taylor et al. [31] and stored in a lecture bottle at room temperature. The CH₃ONO purity (>95%) was verified by GC/MS.

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

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): cyclohexane (99.9%), hexane (99%), 2,5dimethylfuran (99%), 2,6-dimethyl-7-octen-2-ol (99%), decane (99+%), 2-butanol (99.5%), acetonitrile (99.93%), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (99+%), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%); from Fisher Scientific: methanol (99%); from Spectrum Analytical (New Brunswick, NJ): methylene chloride (99.5%). 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.

Experimental Procedures

The experimental procedures for determining the dihydromyrcenol + OH reaction kinetics were similar

to those described previously [17,18].

Dihydromyrcenol + OH $\xrightarrow{k_{OH+Dihydromyrcenol}}$ Products (4)

Reference + OH
$$\xrightarrow{\kappa_{\text{Ref}}}$$
 Products (5)

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

$$\ln\left(\frac{[\text{Dihydromyrcenol}]_{0}}{[\text{Dihydromyrcenol}]_{t}}\right)$$
$$=\frac{k_{\text{OH}+\text{Dihydromyrcenol}}}{k_{\text{Ref}}} \times \ln\left(\frac{[\text{Ref}]_{0}}{[\text{Ref}]_{t}}\right) \quad (6)$$

If reaction with OH is the only removal mechanism for dihydromyrcenol and reference, a plot of $\ln[[dihydromyrcenol]_0/[dihydromyrcenol]_t)$ versus $\ln([Ref]_0/[Ref]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{OH+dihydromyrcenol}$ (Fig. 1). The OH rate constant experiments for dihydromyrcenol employed the use of three reference compounds: decane, 2-butanol, and 2,5-dimethylfuran. The use of three different reference compounds with different OH rate constants more definitively assured the accuracy of the dihydromyrcenol/OH rate constant and demonstrates that other reactions are not removing dihydromyrcenol. Typically five experimental runs were conducted on each dihydromyrcenol/reference pair.

For the dihydromyrcenol/OH kinetic experiments, the typical concentrations of the pertinent species in the Teflon chamber were 0.3-0.6 ppm (0.7- 1.4×10^{13} molecule cm⁻³) dihydromyrcenol, 0.5– 0.7 ppm $(1.2-1.6 \times 10^{13} \text{ molecule cm}^{-3})$ reference, 10 ppm (23×10^{13} molecule cm⁻³) CH₃ONO, and 0– 0.6 ppm $(0-1.4 \times 10^{13} \text{ molecule cm}^{-3})$ NO in air. Dihydromyrcenol was diluted in a 25:75 (v:v) solution with methanol. Methanol was chosen because both the methanol/OH and methanol/O3 rate constants and reaction products were not expected to affect the experimental results. These mixtures were allowed to reach equilibrium before initial species concentration $([X]_0)$ samples were collected. Typically, four photolysis intervals of 10-20 s each were used on the reaction mixture for a combined total photolysis time of approximately 40-60 s. The total ion chromatogram (TIC) from the Agilent 5973 mass selective detector was used to determine dihydromyrcenol and reference concentrations.

The experimental methods and parameters for observation of dihydromyrcenol/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 10–20 s intervals followed by sample collection. When possible, commercially available samples of the identified products were analyzed to verify matching ion spectra and chromatographic retention times.

The experimental procedures for the determination of the dihydromyrcenol $+ O_3$ reaction kinetics were





Figure 1 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol) relative rate plot with decane (\blacklozenge), 2,5-dimethyl furan (Δ), and 2-butanol (\Box) as reference compounds. The OH + dihydromyrcenol rate constant, $k_{dihydromyrcenol + OH}$, measured is (37.7 ± 0.8) × 10⁻¹² cm³ molecule⁻¹ s⁻¹.

similar to those described previously [32].

Dihydromyrcenol + O₃
$$\xrightarrow{k_{O_3 + \text{Dihydromyrcenol}}}$$
 Products (7)

Ozone was injected into the reaction chamber as it was being filled with air and dihydromyrcenol. The range of dihydromyrcenol concentrations was 0.3-1.2 ppm $(0.7-2.9 \times 10^{13} \text{ molecule cm}^{-3})$ with an initial O₃ concentration of 0.1 ppm $(0.2 \times 10^{13} \text{ molecule cm}^{-3})$. Cyclohexane (410 ppm) was also injected into the reaction chamber to scavenge any OH formed as a byproduct of the dihydromyrcenol/O₃ reaction [33]. The chamber was transferred within 5 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. In these series of experiments, no decrease in O₃ concentration was observed over the reactant concentration range.

In order to determine an upper limit estimate for the dihydromyrcenol/ O_3 reaction rate constant, both dihydromyrcenol and O_3 concentrations were increased to 2.8 ppm and 0.3 ppm, respectively. As before, O_3 was injected into the reaction chamber as it was being filled with air and dihydromyrcenol.

Derivatization of the carbonyl reaction products was initiated by flowing of 15 to 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, ketone, and dicarbonyl reaction products to oximes [25] over a 24-48 h time period in the dark. The reacted solutions were gently blown to dryness with UHP N₂, reconstituted with 100 µL of methanol, and 1 μ L 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 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 silvlation, and then 1 μ L of the solution was injected into the Varian 3800/Saturn 2000 GC/MS system [25]. Additionally, chemical ionization (CI) mass spectra using acetonitrile were also collected on the derivatized reaction products allowing the determination of the PFBHA or PFBHA/BSTFAderivatized compound's molecular weight.

To determine possible chromatographic interferences from reference/OH reaction products, both dihydromyrcenol and the reference compounds were reacted with the OH radical in separate experiments and analyzed as described above. No chromatographic interferences were observed. Two experiments were conducted to determine the stability of the reference and dihvdromyrcenol coexisting in the same chamber. First, the reference and dihydromyrcenol were injected into the chamber, analyzed, photolyzed for 6 min and reanalyzed. In a separate experiment, methyl nitrite, NO, reference, and dihydromyrcenol were injected into the chamber, analyzed, left 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 chamber was cleaned by flushing the chamber six times with air (<0.1 ppm total)hydrocarbon). Measurements of an air-filled chamber 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

Dihydromyrcenol/OH Reaction Rate Constant

The OH rate constant for 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol, Structure 1) was obtained using the relative rate method described above. The plot of a modified version of Eq. (6) is shown in Fig. 1. The $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ term is divided by the respective reference rate constant (decane $(11.0 \pm 0.28) \times$ 10^{-12} cm³ molecule⁻¹ s⁻¹), 2,5-dimethyl furan (132 \pm $33) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹), and 2-butanol $(8.65 \pm 2.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ [10,11,18, 34] and multiplied by 10^{-12} cm³ molecule⁻¹ s⁻¹, resulting in a unitless number. This yields a slope that is equal to the OH radical/dihydromyrcenol rate constant, $k_{OH+dihydromyrcenol}$, divided by 10^{-12} cm³ molecule $^{-1}$ s $^{-1}$. This modification allows for a direct comparison of the three reference compound/ dihydromyrcenol data sets. The slope of the line shown in Fig. 1 yields an OH radical bimolecular rate constant, $k_{OH+dihydromyrcenol}$, of $(37.7 \pm$ $(0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The data points at the origin are experimental points because preirradiation, t = 0, data showed no detectable loss of dihydromyrcenol or reference. The error in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate

constants ($\pm 25\%$ for decane, 2,5-dimethylfuran, and 2-butanol) used to derive the dihydromyrcenol/OH rate constant yields a final value for $k_{\text{OH}+\text{dihydromyrcenol}}$, of $(38 \pm 9) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ [10,11,34].

The dihydromyrcenol/OH rate constant, $k_{OH+dihydromyrcenol}$, has not been previously reported. The observed rate constant can be compared to a $k(calc)_{OH+dihydromyrcenol} = 37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, calculated using the Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91 [35].

Dihydromyrcenol/O₃ Reaction Rate Constant

The experimental conditions, described above, to determine the dihydromyrcenol/O₃ reaction rate constant yielded a first-order decrease in ozone concentration over a 15 min monitoring period. Analysis of the data resulted in an upper limit determination of the dihydromyrcenol/O₃ rate constant of 2×10^{-18} cm³ molecule⁻¹ s⁻¹. The dihydromyrcenol/O₃ rate constant, $k_{O_3+dihydromyrcenol}$, has not been previously reported. The estimated rate constant can be compared with a $k(\text{calc})_{O_3+dihydromyrcenol}$, =1.2 $\times 10^{-17}$ cm³ molecule⁻¹ s⁻¹, calculated using the Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91 [35].

Dihydromyrcenol/OH and Dihydromyrcenol/O₃ Reaction Products

The reaction products observed from the initial dihydromyrcenol/OH hydrogen abstraction or OH addition to the carbon-carbon double bond are consistent with previously observed OH radical reaction mechanisms for oxygenated organic species [12–19]. Typically, the oxygenated organic parent compound reacts with OH to subsequently generate other oxygenated organic products. For dihydromyrcenol, the dihydromyrcenol/OH reaction products observed and positively identified, using the pure compound for verification by either direct gas-phase detection or derivatization or both, were acetone, 2-methylpropanal (O=CHCH(CH₃)₂), 2methylbutanal (O=CHCH(CH₃)CH₂CH₃), ethanedial (glyoxal, HC(=O)C(=O)H), 2-oxopropanal (methylglyoxal, $CH_3C(=O)C(=O)H$), and are listed in Table I. Many other dihydromyrcenol/OH reaction products were observed utilizing the derivatization methods described above. Elucidation of these other reaction products was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible dihydromyrcenol/OH reaction mechanisms based on previously published volatile organic compound/OH gas-phase reaction mechanisms [10,12–19]. These other reaction products are listed in Table I.

The results for both the positively identified reaction products and the other observed reaction products are described below.

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 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 ([CH₂C₆F₅]⁺ fragment) with a large relative intensity (>40%) and a [PFBHA oxime + $[181]^+$ ion (due to reactions in the ion trap mass spectrometer) [25]. In most cases, the m/z 181 ion relative intensity for the chromatographic peaks due to dihydromyrcenol/OH and dihydromyrcenol/O3 reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms [25]. The mass spectra of compounds that were additionally derivatized with BSTFA contained m/z 73 ions from the [Si(CH₃)₃]⁺ fragments [25]. The product data are described below.

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 dihydromyrcenol concentration and were observed only after OH initiation of dihydromyrcenol/methanol/methyl nitrite/NO/air mixtures or addition of O₃ to dihydromyrcenol/methanol/air. Derivatization experiments performed in the absence of dihydromyrcenol 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 below except for small amounts (as noted by chromatographic peak areas) of acetone, 2-methylpropanal, 2-methylbutanal, 2-oxopropanal, and ethanedial. Acetone was also observed in prephotoinitiated dihydromyrcenol/OH or preozonated dihydromyrcenol/O3 derivatization samples. However, the acetone, 2oxopropanol, and ethanedial oxime peak areas increased significantly, from 30% to 65%, with dihydromyrcenol/OH reaction initiation, indicating that acetone, 2-oxopropanal, and ethanedial are likely products of the dihydromyrcenol + OH reaction. Increases in both 2-oxopropanal and ethanedial peak areas with dihydromyrcenol/O₃ reaction initiation indicated that

Retention Time (min)	Name	Molecular Weight (amu)	Structure	CI Ions Observed	EI Ions Observed (Relative Intensity %)
11.4	Acetone	58	, o	254	181(100), 223(20), 253(14)
12.5 12.6	2-Methylpropanal	72	٩	268	181(100), 250(60)
13.6	2-Methylbutanal	86	•	282	55(27), 181(100), 264(80)
14.1 14.4	Glycolaldehyde	60	НО	256	57(8–32), 69(15), 97(15), 127(15), 161(10), 181(100), 195(17), 206(10), 225(15), 226(22)
15.9	2-Methylbut-3-enal	84		280	59(100), 181(97), 239(60), 282(24)
16.3	4-Methylhex-5-enal	112		308 : 0	55(16), 95(12), 126(20), 181(100), 239(10)
17.4	3-Methylpent-4-enal	98		294	59(35), 130(42.5), 181(100), 294(12.5)
18.1 18.2 19.5 19.7	2,6-Dimethylhept-5-ena	1 140		336	41(28), 59(57–65), 72(62), 112(5–25), 154(15–22), 181(48–100), 253(30–100), 266(27–42), 336(5–17), 429(32)
21.0 21.2	Ethanedial	58	/ °	449	181(100), 448(28)
21.5	2-Oxopropanal	72	o' o	463	181(100), 265(34), 462(7.5)

 Table I
 Molecular Structure of Some Dihydromyrcenol/OH Reaction Products

they are likely reaction products. Acetone is also a product of the dihydromyrcenol/O₃ reaction, but its peak area increased by only a few percent. Aside from the positively identified reaction products (Table I) with the synthesis of the derivatized oxime compound, dihydromyrcenol/OH and dihydomyrcenol/O₃ reaction product identification was derived from mass spectra data and previously published VOC/OH and VOC/O₃ reaction mechanisms [12–19,25].

Acetone

Acetone was identified using the Agilent 6890/5973 GC/MS system and PFBHA derivatization method

described above. The acetone oxime (PFBHA= $C(CH_3)_2$) was observed at approximately 11.4 min employing the Varian 3800/Saturn 2000 GC/ion trap mass spectrometer system described above. Acetone oxime was synthesized to confirm this chromatographic assignment. Acetone oxime was observed in prephotolysis samples, but the peak area increased upon initiation of dihydromyrcenol/OH reaction indicating acetone as a dihydromyrcenol/OH reaction product. Acetone was also identified as a dihydromyrcenol/O₃ reaction product.

2-Methylpropanal (O=CHCH(CH₃)₂)

The chromatographic peaks for the oxime observed at 12.5 and 12.6 min were observed as a reaction product of dihydromyrcenol/OH and had ions at m/z (relative intensity) 181 (100%) and 250 (60%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 268 was observed for the PFBHA-derivatized sample. The 2-methylpropanal oxime was synthesized to confirm this chromatographic assignment. This carbonyl compound was also observed as a dihydromyrcenol/O₃ reaction product.

2-Methylbutanal (O=CHCH(CH₃)CH₂CH₃)

The single chromatographic peak for the oxime observed at 13.6 min was observed as a reaction product of dihydromyrcenol/OH and had ions at m/z (relative intensity) 55 (27%), 181 (100%), and 264 (80%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 282 was observed for the PFBHAderivatized sample. The 2-methylbutanal oxime was synthesized to confirm this chromatographic assignment. This carbonyl compound was also observed as a dihydromyrcenol/O₃ reaction product.

Oxime at Retention Time 14.1 and 14.4 min

The oxime observed with a chromatographic peak at a retention time of 14.1 and 14.4 min had ions of m/z (relative intensity) 57 (8–32%), 69 (15%), 97 (15%), 127 (15%), 161 (10%), 181 (100%), 195 (17%), 206 (10%), 225 (15%), 226 (22%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 256 was observed. Using the derivatized molecular weight of 255 for the oxime suggests a carbonyl compound with a molecular weight of 60. A proposed dihydromyrcenol/OH reaction product assignment of glycolaldehyde (see Table I) was made based upon the observed data.

Oxime at Retention Time 15.9 min

The oxime observed with a chromatographic peak at a retention time of 15.9 min had ions of m/z (relative intensity) 59 (100%), 181 (97%), 239 (60%), and 282 (24%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 280 was observed. Using the derivatized molecular weight of 279 for the oxime suggests a carbonyl compound with a molecular weight of 84. The single chromatographic peak suggests an aldehyde structure or a symmetric ketone structure. A proposed dihydromyrcenol/OH reaction product assignment of 2-methylbut-3-enal (see Table I) was made based upon the observed data.

Oxime at Retention Time 16.3 min

The oxime observed with a chromatographic peak at a retention time of 16.3 min had ions of m/z (relative intensity) 55 (16%), 95 (12%), 126 (20%), 181 (100%), and 239 (10%) as seen in Fig. 2A. This reaction product chromatographic peak was the largest one observed for the dihydromyrcenol/OH reaction. Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 308 was observed as seen in Fig. 2B. Using the derivatized molecular weight of 307 for the oxime suggests a carbonyl compound with a molecular weight of 112. The single chromatographic peak suggests an aldehyde structure or a symmetric ketone structure. A proposed dihydromyrcenol/OH reaction product assignment of 4-methylhex-5-enal (see Table I) was made based upon the observed data.

Oxime at Retention Time 17.4 min

The oxime observed with a chromatographic peak at a retention time of 17.4 min had ions of m/z (relative intensity) 59 (35%), 130 (42.5%), 181 (100%), and 294 (12.5%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 294 was observed. Using the derivatized molecular weight of 293 for the oxime suggests a carbonyl compound with a molecular weight of 98. The single chromatographic peak suggests an aldehyde structure or a symmetric ketone structure. A proposed dihydromyrcenol/OH reaction product assignment of 3-methylpent-4-enal (see Table I) was made based upon the observed data.

Oxime at Retention Time 18.1, 18.2, 19.5, 19.7 min

The oxime observed with chromatographic peaks at retention times of 18.1, 18.2, 19.5, and 19.7 min was observed as a reaction product of dihydromyrcenol/OH



Figure 2 PFBHA-derivatized product of dihydromyrcenol (16.3 min) (A) electron ionization spectrum (B) acetonitrile chemical ionization spectrum.

and had ions of m/z (relative intensity) 41 (28%), 59 (57–65%), 72 (62%), 112 (5–25%), 154 (15–22%), 181 (48–100%), 253 (30–100%), 266 (27–42%), 336 (5–17%), and 429 (32%). Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 336 was observed for the PFBHA-derivatized sample. Using the derivatized molecular weight of 335 for the oxime suggests a carbonyl compound with a molecular weight of 140. A proposed dihydromyrcenol/OH reaction product assignment of 2,6-dimethylhept-5-enal (see Table I) was made based upon the observed data. This carbonyl compound was also observed as a dihydromyrcenol/O₃ reaction product.

Ethanedial (Glyoxal, HC(=O)C(=O)H)

The chromatographic peaks for the oxime observed at 21.0 and 21.2 min were observed as reaction products of dihydromyrcenol/OH and had ions at m/z (relative intensity) 181 (100%) and 448 (28%). The m/z 448 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight

of 58. Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 449 was observed for the PFBHAderivatized sample. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment. This carbonyl compound was also observed as a dihydromyrcenol/O₃ reaction product.

2-Oxopropanal (Methylglyoxal, CH₃C(=O)C(=O)H)

The single peak for the oxime observed at 21.5 min was observed as a reaction product of dihydromyrcenol/OH and had ions at m/z (relative intensity) 181 (100%), 265 (34%), and 462 (8%). The m/z 462 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 72. Using acetonitrile for chemical ionization, an M + 1 ion of m/z of 463 was observed for the PFBHA-derivatized sample The PFBHA-methylglyoxal oxime was synthesized to confirm this chromatographic assignment, and the second chromatographic peak for PFBHA-methylglyoxal overlaps with the 21.2 min peak of

PFBHA-glyoxal. This carbonyl compound was also observed as a dihydromyrcenol/O₃ reaction product.

DISCUSSION

OH reacts with dihydromyrcenol by H-atom abstraction or OH addition to the carbon-carbon double bond [7]. The "reactive structure" of dihydromyrcenol can be drawn as shown in Structure 1. Dihydromyrcenol is a molecule with seven distinct sites for possible hydrogen abstraction and one site for OH addition. However, the sites labeled I, II, and III identified in Structure 1 contribute approximately 71%, 4%, and 12%, respectively, to the calculated dihydromyrcenol/OH rate constant of 37×10^{-12} cm³ molecule⁻¹ s⁻¹ [21]. This calculated value is in very good agreement with the measured value reported here $((38 \pm 9) \times$ $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), considering that OH rate constants calculated using structure reactivity are typically within a factor of two of the measured OH rate constant [21].

For the dihydromyrcenol/OH reaction, the experimental parameters were set to minimize other side reactions and highlight the first OH hydrogen abstraction and OH addition step. The dihydromyrcenol concentration was kept low, and the photolysis times were as short as possible. Additionally, nitric oxide (NO) was added to facilitate the generation of OH and to minimize O_3 and NO_3 formation, preventing other possible radical reactions. The possible mechanistic steps leading to product formation are described below. Depending on the nature of the radicals formed in reactions (4) and (7), some reaction products may be formed by multiple pathways.

Acetone

The dihydromyrcenol/OH reaction mechanism has several potential pathways leading to acetone $(O=C(CH_3)_2)$ formation. OH can react with dihydromyrcenol by hydrogen abstraction from site III and subsequent addition of oxygen resulting in the dissociation of the HOC(•)(CH_3)_2 radical leaving the peroxyradical H₂C=CHCH(CH₃)CH₂CH₂CH(OO)•. The HOC(•)(CH₃)₂ radical can then react with oxygenyielding acetone and HO₂. Acetone product formation from the dihydromyrcenol/O₃ reaction is less straightforward and may involve isomerization [36].

4-Methylhex-5-enal

The chromatographic peak proposed to be 4methylhex-5-enal, based on mass spectral data, was the largest product peak observed in the PFBHA derivatization experiments from the dihydromyrcenol/OH reaction. 4-Methylhex-5-enal is likely formed from OH hydrogen abstraction from site III. After hydrogen abstraction an oxygen molecule adds to the radical forming a β -hydroxyalkyl radical. Subsequent reaction with oxygen and NO yields the β -hydroxyalkoxy radical (RO•) which results in 4-methylhex-5-enal and NO₂.

$H_2C = CHCH(CH_3)CH_2CH_2CH_2C(CH_3)_2OH + OH$					
$\rightarrow H_2C=CHCH(CH_3)CH_2CH_2CH_{\bullet}C(CH_3)_2OH$					
$+ H_2O$ (8)					
$H_2C = CHCH(CH_3)CH_2CH_2CH \bullet C(CH_3)_2OH + O_2$					
$\rightarrow H_2C=CHCH(CH_3)CH_2CH_2CH(OO)\bullet C(CH_3)_2OH$					
(9)					
$H_2C=CHCH(CH_3)CH_2CH_2CH(OO)\bullet C(CH_3)_2OH$					
$+ \text{NO} \rightarrow \text{NO}_2 + \text{H}_2\text{C=CHCH(CH_3)CH}_2\text{CH}_2\text{CH}(\text{O})$					
•C(CH ₃) ₂ OH (10)					
$H_2C = CHCH(CH_3)CH_2CH_2CH(O) \bullet C(CH_3)_2OH$					
\rightarrow beta scission $\rightarrow \underline{H_2C=CHCH(CH_3)CH_2CH_2}$					
$\underline{CH=O} + \bullet C(CH_3)_2OH (11)$					

Recently, PFBHA-coated solid-phase microextraction (SPME) fibers were used for the passive sampling of the gas-phase reaction products of Z-3-hexen-1ol/OH, 2-methyl-3-buten-2-ol/OH, and a series of diols/OH. These reactions yielded products that supported OH addition to carbon-carbon double bond and hydrogen abstraction from the C-H bonds of HC(OH) groups [37,38]. However, if OH added to the dihydromyrcenol carboncarbon double bond (site I) an expected reaction product would be 6-hydroxy-2,6-dimethylheptanal (O=CHCH(CH₃)CH₂CH₂CH₂C(CH₃)₂OH). Unfortunately, it was not observed in the experimental system described above. Long chained alcohol carbonyls have been observed previously from our laboratory using the described derivatization techniques highlighting that if 6-hydroxy-2,6-dimethylheptanal were formed as a reaction product it would most likely have been detected [20]. This expected reaction product could adhere to the Teflon surface or be incorporated into ultrafine particulate matter and thus escape described detection methods. Another possible reason for not observing 6hydroxy-2,6-dimethylheptanal is that once the OH adds to the double bond there are possible fragmentation pathways or isomerization leading to other observed products. It is likely that both glycolaldehyde (Table I) and 2,6-dimethylhept-5-enal (Table I) are the result of OH addition to the carbon–carbon double bond. A possible mechanism for the formation of these two products is shown in Fig. 3. However, the formation of 4-methylhex-5-enal and acetone as the major hydrogen abstraction products, based on chromatographic peak area, was consistent with structure–reactivity calculations [35]. Several of the possible reaction products could be formed by isomerization of the alcoholic hydrogen due to the length of the carbon chain backbone of dihydromyrcenol [36].

Ozone reacts with dihydromyrcenol by addition to the carbon-carbon double bond (site I, Structure 1). The calculated dihydromyrcenol/ O_3 rate

constant using Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91, is 1.2×10^{-17} cm³ molecule⁻¹ s⁻¹ [35]. This value is approximately six times faster than the experimentally estimated upper limit value of 2×10^{-18} cm³ molecule⁻¹ s⁻¹. The difference between the estimated and calculated dihydromyrcenol/O₃ rate constant (~600%) is significant when compared to the difference between the measured and calculated dihydromyrcenol/OH rate constant of ~3%. This suggests that the interaction between dihydromyrcenol and O₃ is not accurately described by AOPWIN v1.91.



Figure 3 Proposed mechanism for OH addition to dihydromyrcenol carbon–carbon double bond.

The reaction products observed from dihydromyrcenol/O₃ reaction are due solely to ozone reacting with dihydromyrcenol and not due to secondary OH formed from dihydromyrcenol/O₃ reacting with dihydromyrcenol. The primary dihydromyrcenol/OH reaction product—the carbonyl product observed as the 16.3 min oxime and tentatively identified as 4-methylhex-5-enal—was not observed in the dihydromyrcenol/O₃ experiments.

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 molecular structure of the dihydromyrcenol/OH and dihydromyrcenol/O₃ reaction products.

CONCLUSIONS

In order to investigate the detailed gas-phase chemistry of 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol, Structure 1), the hydroxyl (OH) radical reaction rate constant, ozone reaction rate constant, and respective reaction mechanisms were determined. The OH radical can either abstract hydrogen or add to the carbon–carbon double bond of dihydromyrcenol. A bimolecular rate constant, $k_{OH+dihydromyrcenol}$, of (38 ± 9) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ was measured using the relative rate technique. Ozone is expected to add to the carbon–carbon double bond of dihydromyrcenol. An upper limit of 2×10^{-18} cm³ molecule⁻¹ s⁻¹ was determined for $k_{O_3+dihydromyrcenol}$.

The identification of the dihydromyrcenol/OH and dihydromyrcenol/O₃ reaction products was facilitated by the use of derivatizing agents PFBHA and BSTFA. While many dihydromyrcenol/OH reaction products were simply proposed based on observed experimental data and previously published VOC/OH reaction mechanisms, several reaction products such as acetone, 2-methylpropanal, 2-methylbutanal, ethanedial, and 2-oxopropanal were positively identified. The structures of the identified reaction products indicate that the carbon–carbon double bond and the secondary hydrogen of a carbon next to a carbon with an alcohol group play important roles in the formation of dihydromyrcenol/OH and dihydromyrcenol/O₃ reaction products.

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