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Gas-phase chemistry of citronellol with ozone and OH radical: Rate constants and products

Jason E. Ham[a], Steven P. Proper[b], J.R. Wells[a,*]

[a]*Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Road, Morgantown, WV 26505, USA*
[b]*Department of Science and Mathematics, Environmental Chemistry, Kettering University, 1700 West Third Avenue, Flint, MI 48504, USA*

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Abstract

A bimolecular rate constant, $k_{\mathrm{OH+citronellol}}$, of $(170\pm43)\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ was measured using the relative rate technique for the reaction of the hydroxyl radical (OH) with 3,7-dimethyl-6-octen-1-ol (citronellol) at (297 ± 3) K and 1 atmosphere total pressure. Additionally, a bimolecular rate constant, $k_{\mathrm{O_3+citronellol}}$, of $(2.4\pm0.1)\times10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, was measured by monitoring the decrease in ozone (O_3) concentration in an excess of citronellol. To more clearly define part of citronellol's indoor environment degradation mechanism, the products of the citronellol + OH and citronellol + O_3 reactions were also investigated. The positively identified citronellol/OH and citronellol/O_3 reaction products were: acetone, ethanedial (glyoxal, HC(=O)C(=O)H), and 2-oxopropanal (methylglyoxal, $CH_3C(=O)C(=O)H$). The use of derivatizing agents *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were used to propose 6-hydroxy-4-methylhexanal as the other major citronellol/OH and citronellol/O_3 reaction product. The elucidation of this other reaction product was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible citronellol/OH and citronellol/O_3 reaction mechanisms based on previously published volatile organic compound/OH and volatile organic compound/O_3 gas-phase reaction mechanisms.
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Keywords: Citronellol; 3,7-dimethyl-6-octen-1-ol; Reaction products; Kinetics; Oxygenated organic compounds

1. Introduction

In the USA, 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 (Delfino, 2002; Mendell et al., 2002). 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 (Bodin et al., 2003; Kreiss et al., 2002; Nielsen, 1991; Rohr et al., 2002; Wilkins et al., 2001; Wolkoff et al., 1999, 2000). There is growing interest in understanding the role volatile organic compound (VOC) gas-phase reaction products have on human health (Doyle et al., 2004; Sexton et al., 2004; Weschler and Wells, 2004).

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*Corresponding author. Tel.: +1 304 285 6341; fax: +1 304 285 6041.
E-mail address: ozw0@cdc.gov (J.R. Wells).

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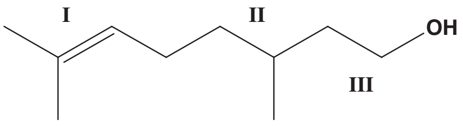
A recent review of indoor environment chemistry by Weschler highlights several research areas important to the field (Weschler, 2001). Significant observations from this review paper are that there are still several fundamental questions regarding the gas-phase chemistry of indoor environments, and that the indoor environment is chemically more complex than previously thought. Experimental evidence has demonstrated that several initiator species such as ozone (O_3), hydroxyl radical (OH) and nitrate radical (NO_3) are likely to be present in indoor air and the VOC concentrations indoors are higher by a factor of ten or more than typically found in outdoor environments (Weschler, 2001; Weschler and Shields, 1997a).

Oxygenated organic compounds, such as ethers, alcohols and esters, are becoming more prevalent in the indoor environment as they are substituted for other chemicals in consumer products. One such compound of interest is 3,7-dimethyl-6-octen-1-ol (citronellol, Structure 1) a volatile organic alcohol that is a significant component of bug/insect repellants and hard-surface cleaners (International Flavors Fragrances and Inc., 2005; Nazaroff and Weschler, 2004). While several hydroxyl radical (OH) + oxygenated organic and ozone (O_3) + oxygenated organic bimolecular rate constants are well known (Atkinson, 1989, 1994), a few recent studies of the products from OH + oxygenated organic reactions have illustrated the complexity of their gas-phase reaction mechanisms (Andersen et al., 2005; Bradley et al., 2001; Smith et al., 1992, 1995; Veillerot et al., 1996; Wallington et al., 1993, 2001; Wells, 2004; Wells et al., 1996; Wyatt et al., 1999). These investigations are needed to support hydroxyl radical and ozone reaction mechanism patterns based on chemical structure-reactivity relationships (Boethling and Mackay, 2000).

In the work presented here, the rate constant of the OH radical with citronellol was measured by the relative rate method. Additionally, the citronellol/O_3 rate constant was also determined by monitoring the decrease in the ozone concentration in an excess of citronellol (Atkinson et al., 1981). The products of the OH + citronellol and O_3 + citronellol reactions are also reported. Neither the OH rate constant, O_3 rate constant nor the respective reaction products for citronellol have been reported previously.



Structure 1. 3,7-Dimethyl-6-octen-1-ol.

2. Experimental methods

2.1. Apparatus and materials

Experiments to measure the gas-phase rate constant of the OH + 3,7-dimethyl-6-octen-1-ol (citronellol, Structure 1) reaction were conducted with a previously described apparatus (Wells, 2004). Sampling for the citronellol/OH kinetics experiments was performed using a polydimethylsolixane/divinylbenzene solid phase micro-extraction (SPME) fiber (Supelco, Milwaukee, WI, 57310-U) assembly which was inserted into a 6.4 mm Swagelok (Solon, OH) fitting attached to a 60–90 L Teflon$^{®}$-film chamber. The SPME fiber was exposed for 5 min within the chamber, and then inserted into the injector of a Hewlett Packard (HP) 5890 gas chromatograph with a 5972 mass selective detector (GC/MS) and HP software. The GC temperature program used was: injection port was set to 250 °C, and oven temperature began at 40 °C for 6 min and was ramped 10 °C min^{-1} to 260 °C and held for 3 min. Experiments to measure the reaction of ozone with 3,7-dimethyl-6-octen-1-ol were conducted using a similar chamber as described above, except the ozone concentration was monitored using a UV photometric ozone analyzer (Thermo Environmental model 49-C Franklin, MA).

Identification of reaction products was made using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to derivatize carbonyl products, while alcohol and carboxylic acid products were derivatized using PFBHA and BSTFA (Fick et al., 2003; Yu et al., 1998). Experimental methods for reaction product identification were similar to methods used for kinetic experiments, except the reference compound was excluded from the reaction mixture.

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 (Yu et al., 1998). 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^{-1} 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^{-1} to 250 °C and held to the end of the chromatographic run (Yu et al., 1998). The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from *m/z* 40–650. 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.

Hydroxyl radicals, which are among the primary oxidizing radicals in the indoor environment (Sarwar et al., 2002; Sexton et al., 2004; Weschler and Shields, 1996, 1997b), were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide (NO) in air (Atkinson et al., 1981). CH_3ONO was prepared in gram quantities using the method of Taylor et al. (1980) and stored in a lecture bottle at room temperature. The CH_3ONO 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%), limonene (99%), 3,7-dimethyl-6-octen-1-ol (citronellol) (99%), 3-carene (90%), acetonitrile (99.93%), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (99+%), *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) (98+%); from Fisher Scientific (Fairlawn, NJ): 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 atmosphere pressure.

2.2. Experimental procedures

The experimental procedures for determining the citronellol+OH reaction kinetics were similar to those described previously (Bradley et al., 2001; Wells, 2004; Wyatt et al., 1999).

$$\text{Citronellol} + \text{OH} \xrightarrow{k_{\text{OH+Citronellol}}} \text{Products}, \quad (1)$$

$$\text{Reference} + \text{OH} \xrightarrow{k_{\text{Ref}}} \text{Products}. \quad (2)$$

The rate equations for reactions 1 and 2 are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\text{Citronellol}]_0}{[\text{Citronellol}]_t}\right) = \frac{k_{\text{OH+Citronellol}}}{k_{\text{Ref}}} \ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right). \quad (3)$$

If reaction with OH is the only removal mechanism for citronellol and reference, a plot of $\ln([\text{Citronellol}]_0/[\text{Citronellol}]_t)$ versus $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{\text{OH+citronellol}}$ (Fig. 1). The OH rate constant experiments for citronellol employed the use of two reference compounds: limonene and 3-carene. The use of two different reference compounds with different OH rate constants more definitively assured the accuracy of the citronellol/OH rate constant and demonstrates that other reactions are not removing citronellol.

For the citronellol/OH kinetic experiments the typical concentrations of the pertinent species in the 60–90 L Teflon chamber were 0.3–0.7 ppm ($0.7–1.7 \times 10^{13}$ molecule cm^{-3}) citronellol, 0.3–0.6 ppm ($0.7–1.5 \times 10^{13}$ molecule cm^{-3}) reference, 10 ppm (23×10^{13} molecule cm^{-3}) CH_3ONO, and 0–0.6 ppm ($0–1.4 \times 10^{13}$ molecule cm^{-3}) NO in air. Citronellol was diluted

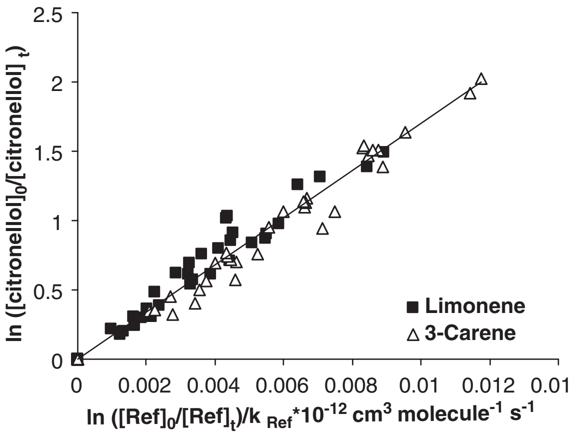


Fig. 1. 3,7-Dimethyl-6-octen-1-ol (citronellol) relative rate plot with limonene (■) and 3-carene (△) as reference compounds. The OH+Citronellol rate constant, $k_{\text{OH+Citronellol}}$, measured is $(170\pm4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

in a 30:70 (v:v) solution with methanol. Methanol was chosen because the methanol/OH reaction did not yield chromatographically interfering products. Furthermore, for the methanol/O_3 reaction, methanol does not react with O_3 because of the absence of a double bond. The gas-phase 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 HP 5972 mass selective detector was used to determine citronellol and reference concentrations.

The experimental procedures for the determination of the citronellol + O_3 reaction kinetics were similar to those described previously (Atkinson and Aschmann, 1984).

$$\text{Citronellol} + O_3 \overset{k_{O_3+\text{Citronellol}}}{\longrightarrow} \text{Products.} \quad (4)$$

Approximately 0.1 ppm (2.46×10^{12} molecule cm^{-3}) of ozone was injected into the reaction chamber as it was being filled with air and citronellol. The range of initial citronellol concentrations was 0.2–0.6 ppm (0.4–1.5×10^{13} molecule cm^{-3}). The chamber was connected 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 420 s. Cyclohexane (410 ppm, 4.1×10^{18} molecules cm^{-3}) was added to the citronellol/O_3 reaction product experiments to scavenge OH radicals (Paulson et al., 1999).

Derivatization of the carbonyl reaction products was initiated by 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 the carbonyl reaction products to oximes (Yu et al., 1998) over a 24–48 h time period in the dark. The reacted solutions were gently blown to dryness with UHP N_2, 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 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 (Yu et al., 1998).

To determine possible chromatographic interferences from reference/OH reaction products, both citronellol and the reference compounds were reacted with the OH radical in separate experiments and analyzed as described previously (Wells, 2004). No chromatographic interferences were observed. All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 3.4% was achieved with the described sampling methods utilizing the HP 5890/5972 GC/MS system.

3. Results

3.1. Citronellol/OH reaction rate constant

The OH rate constant for 3,7-dimethyl-6-octen-1-ol (citronellol, 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 (limonene $(164 \pm 41) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and 3-carene $(88 \pm 22) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) (Atkinson, 1989, 1994, 2003; Bradley et al., 2001) and multiplied by 10^{-12} cm^3 molecule^{-1} s^{-1}, resulting in a unitless number. This yields a slope that is equal to the OH/citronellol rate constant, $k_{\text{OH+citronellol}}$, *divided by* 10^{-12} cm^3 molecule^{-1} s^{-1}. This modification allows for a direct comparison of the two reference compound/citronellol data sets. The slope of the line shown in Fig. 1 yields an OH bimolecular rate constant, $k_{\text{OH+citronellol}}$, of $(170 \pm 4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The data points at the origin are experimental points because pre-irradiation, $t = 0$, data showed no detectable loss of citronellol 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 (±25% for limonene and 3-carene) used to derive the citronellol/OH rate constant yields a final value for $k_{\text{OH+citronellol}}$, of $(170 \pm 43) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1989, 1994, 2003). The citronellol/OH rate constant, $k_{\text{OH+citronellol}}$, has not been previously reported. The observed rate constant is comparable to a

$k(\mathrm{calc})_{\mathrm{OH+citronellol}} = 98 \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, calculated using the Environmental Protection Agency's rate constant calculation software, AOP-WIN v1.91 (US Environmental Protection Agency, 2000).

3.2. Citronellol/O_3 reaction rate constant

The experimental conditions, described above, to determine the citronellol/O_3 reaction rate constant resulted in a first order decrease in ozone concentration in excess citronellol over a 7 min monitoring period. Analysis of the data, shown in Fig. 2, resulted in the determination of the citronellol/O_3 rate constant of $(2.4 \pm 0.1) \times 10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. The error in this rate constant is the 95% confidence interval from the random uncertainty in the slope. The estimated rate constant can be compared with a $k(\mathrm{calc})_{\mathrm{O_3+citronellol}} = 4.3 \times 10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, calculated using the Environmental Protection Agency's rate constant calculation software, AOP-WIN v1.91 (US Environmental Protection Agency, 2000).

3.3. Citronellol/OH and citronellol/O_3 reaction products

The reaction products observed from the initial citronellol/OH hydrogen abstraction or OH addition or O_3 addition to the carbon–carbon double bond are listed in Table 1. The citronellol/OH and citronellol/O_3 reaction products observed and positively identified using the pure compound for verification by derivatization were: acetone, ethanedial (glyoxal, HC(=O)C(=O)H), 2-oxopropanal (methylglyoxal, $CH_3C(=O)C(=O)H$). Structures and ions used to identify these compounds are listed in Table 1. Elucidation of the other major reaction product, 6-hydroxy-4-methylhexanal, was facilitated by mass spectrometry of the derivatized reaction product coupled with plausible citronellol/OH and citronellol/O_3 reaction mechanisms based on previously published volatile organic compound/OH and volatile organic compound/O_3 gas-phase reaction as described below (Atkinson, 1989; Bradley et al., 2001; Smith et al., 1992, 1995; Veillerot et al., 1996; Wallington et al., 1993; Wells, 2004; Wells et al., 1996; Wyatt et al., 1999).

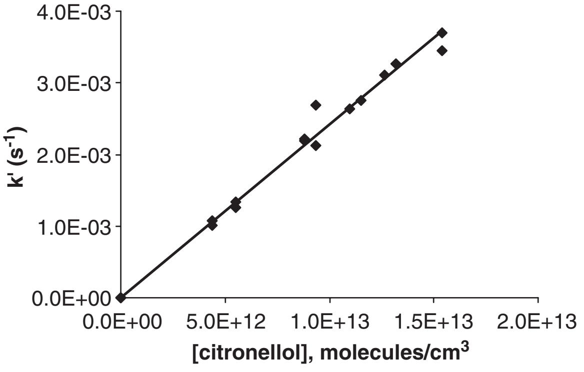
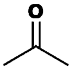
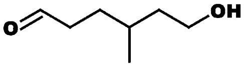
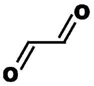
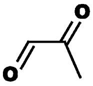


Fig. 2. First order loss rate of ozone versus citronellol concentration. The slope yields a citronellol + ozone reaction rate constant of $(2.4 \pm 0.1) \times 10^{-16}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$.

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 ($[CH_2C_6F_5]^+$ fragment) with a large relative intensity (>40%) and a $[\mathrm{PFBHA\ oxime} + 181]^+$ ion (due to reactions in the ion trap mass spectrometer) (Yu et al., 1998). In most cases, the m/z 181 ion relative intensity for the chromatographic peaks due to citronellol/OH and citronellol/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 (Yu et al., 1998). The mass spectra of compounds that were additionally derivatized with BSTFA contained m/z 73 ions from the $[Si(CH_3)_3]^+$ fragments (Yu et al., 1998). The product data 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 citronellol concentration and were observed only after OH initiation of citronellol/methanol/methyl nitrite/NO/air mixtures or addition of O_3 to citronellol/methanol/air. Derivatization experiments performed in the absence of citronellol, 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-oxopropanal, and ethanedial.

Table 1
Molecular structure of citronellol/OH and citronellol/O_3 reaction products

Retention time (min)	Name	Molecular weight (amu)	Structure	CI ions observed	EI ions observed (relative intensity%)
11.3	Acetone	58		254	181(100), 253(14)
19.67	6-Hydroxy-4-methylhexanal	130		326	181(100), 252(75), 325 (40)
21.0 21.2	Ethanedial	58		449	181(100), 448(33)
21.1 21.4	2-Oxopropanal	72		463	181(100), 265(16), 462 (11)

Acetone was also observed in pre-photoinitiated citronellol/OH or pre-ozonated citronellol/O_3 derivatization samples. However, the acetone, 2-oxo-propanol, and ethanedial oxime peak areas increased significantly, between 30% and 50%, with citronellol/OH or citronellol/O_3 reaction initiation, indicating that acetone, 2-oxopropanal and ethanedial are likely products of the citronellol + OH and citronellol + O_3 reactions.

3.4. Acetone

Acetone was identified as both a citronellol/OH and a citronellol/O_3 reaction product 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 pre-photolysis samples, but the peak area increased upon reaction initiation.

3.5. Oxime at retention time 19.7 min

The oxime observed with chromatographic peak at retention time of 19.7 min had ions of m/z (relative intensity) 84 (19%), 181 (100%), 252 (75%), and 325 (40%). Using acetonitrile for chemical ionization an $M+1$ ion of m/z of 326 was observed. Using the derivatized molecular weight of 325 for the oxime suggests a carbonyl compound with a molecular weight of 130. The single chromatographic peak suggests an aldehyde structure or a symmetric ketone structure. A proposed citronellol/OH and citronellol/O_3 reaction product of 6-hydroxy-4-methylhexanal (see Table 1) was made based upon the observed data. Further confirmation of the proposed identity of this product was made using chemical ionization and PFBHA/BSTFA derivatization. Mass spectra from CI analysis showed two peaks with m/z 398 ($[M+1]$) at 20.1 and 20.2 min, which is the combination of the derivatized PFBHA oxime (m/z 325) with the BSTFA derivatized alcohol (m/z 72).

3.6. Ethanedial (glyoxal, $HC(=O)C(=O)H$)

The chromatographic peaks for the oxime observed at 21.0 and 21.2 min was observed as a reaction product of citronellol/OH and citronellol/O_3 had ions at m/z (relative intensity) 181 (100%), and 448 (33%). 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 PFBHA derivatized sample. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment.

3.7. 2-Oxopropanal (methylglyoxal, $CH_3C(=O)C(=O)H$)

The chromatographic peaks for the oxime observed at 21.1 and 21.4 min was observed as a reaction product of citronellol/OH and citronellol/O_3 had ions at m/z (relative intensity) 181 (100%), 265 (16%), and 462 (11%). 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 21.0 min peak of PFBHA-glyoxal.

4. Discussion

OH reacts with citronellol by H-atom abstraction or OH addition to the carbon–carbon double bond (Atkinson, 1989; Atkinson and Aschmann, 1993). The "reactive structure" of citronellol can be drawn as shown in Structure 1. The sites labeled I, II and III identified in Structure 1 contribute approximately 88%, 3%, and 4%, respectively, to the calculated citronellol/OH rate constant of $98\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ (US Environmental Protection Agency, 2000) which is slower than the measured value reported here $(170\pm43)\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

Ozone reacts with citronellol by addition to the carbon–carbon double bond (site I, Structure 1). The calculated citronellol/O_3 rate constant using Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91 is $4.3\times10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ (US Environmental Protection Agency, 2000) is approximately 2 times faster than the experimentally determined value of $2.4\pm0.1\times10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

For the citronellol/OH reaction the experimental parameters were set to minimize other side reactions and highlight the first OH hydrogen abstraction and OH addition step. The citronellol 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 radical 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 (1) and (4), some reaction products may be formed by multiple pathways.

4.1. Acetone

The citronellol/OH reaction mechanism has several potential pathways leading to acetone ($O{=}C(CH_3)_2$) formation. OH can react with citronellol by addition to the double bond, as seen in Fig. 3. If OH attaches to carbon (C6), this will leave a radical at carbon (C7). Subsequent addition of oxygen to the (C7) radical results in the dissociation of the $OHCH(\bullet)(CH_2)_2CH(CH_3)(CH_2)_2OH$ radical leaving the peroxyradical, $COO(\bullet)(CH_3)_2$. The $COO(\bullet)(CH_3)_2$ radical can then react with NO to form NO_2 and acetone. This reaction is reasonable, since the AOPWIN calculations indicate that OH addition to the double bond accounts for 88% of citronellol's calculated OH rate constant.

Acetone product formation from the citronellol/O_3 reaction is similar to that of the citronellol/OH

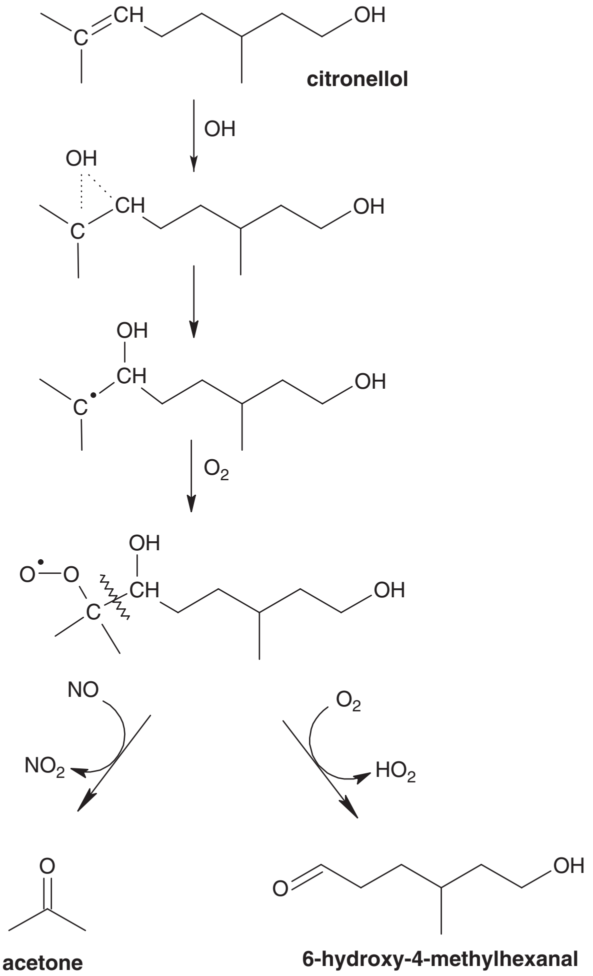


Fig. 3. Reaction mechanism for citronellol + OH showing formation of acetone and 6-hydroxy-4-methylhexanal.

reaction, except that acetone may be formed by two different processes in the same scheme. Ozone adds across the double bond to form a primary ozonide. Subsequent decomposition can occur on either side of this primary ozonide ultimately yielding acetone and (6-hydroxy-4-methylhexanal) $HC(=O)(CH_2)_2CH(CH_3)(CH_2)_2OH$.

4.2. 6-Hydroxy-4-methyhexanal

The chromatographic peak proposed to be 6-hydroxy-4-methylhexanal based on mass spectral data was the largest product peak observed in the PFBHA derivatization experiments from the citronellol/OH and citronellol/O_3 reactions. In the citronellol/OH reaction, 6-hydroxy-4-methylhexanal is likely formed from OH addition to site I, as seen in Fig. 3. OH can add to either side of the double bond. If OH adds to carbon (C_6), the resulting product is the radical, $(CH_3)_2C(\bullet)CH(OH)(CH_2)_2CH(CH_3)(CH_2)_2OH$. Subsequent addition of oxygen to the radical leads to decomposition and formation of the peroxyradical, $(CH_3)_2COO\bullet$ and the radical, $OHCH(\bullet)(CH_2)_2CH(CH_3)(CH_2)_2OH$. This radical reacts with O_2 to form HO_2 and 6-hydroxy-4-methylhexanal, $HC(=O)(CH_2)_2CH(CH_3)(CH_2)_2OH$. This product was also formed in the citronellol/O_3 reaction as described in the acetone section (above).

The reaction products: acetone, ethanedial, 2-oxopropanal, and 6-hydroxy-4-methylhexanal appear in both the citronellol/OH and the citronellol/O_3 reactions. Ozone/alkene reactions can produce steady state OH radical concentrations which would explain the observation of these products in both reactions (Paulson et al., 1999). However, by addition of a large concentration of cyclohexane (410 ppm) in the citronellol/O_3 reaction (which scavenges OH radicals) the citronellol/OH side-reaction is effectively eliminated.

5. Conclusions

In order to investigate the detailed gas-phase chemistry of 3,7-dimethyl-6-octen-1-ol (citronellol, Structure 1), the hydroxyl (OH) radical reaction rate constant, ozone reaction rate constant and respective reaction mechanisms were investigated. The OH radical can either abstract hydrogen or add to the carbon-carbon double bond of citronellol. A bimolecular rate constant, $k_{\mathrm{OH+citronellol}}$, of $(170 \pm 43) \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ was measured using the relative rate technique. Ozone is expected to add to the carbon–carbon double bond of citronellol and a citronellol/O_3 rate constant, $k_{\mathrm{O_3+citronellol}}$, of $(2.4 \pm 0.1) \times 10^{-16}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ was measured.

The identification of the citronellol/OH and citronellol/O_3 reaction products was facilitated by the use of derivatizing agents PFBHA and BSTFA. While many citronellol/OH reaction products were proposed based on previously published VOC/OH reaction mechanisms, reaction products such as acetone, ethanedial, and 2-oxopropanal were positively identified using the observed experimental data. The major reaction product, 6-hydroxy-4-methylhexanal, was proposed based on mass spectral data from the PFBHA and BSTFA experiments and published mechanisms. The structures of the identified reaction products indicate that the carbon–carbon double bond (citronellol/O_3 and citronellol/OH) and the secondary hydrogen of a carbon next to a carbon with an alcohol group (citronellol/OH) play important roles in the formation of reaction products.

Approximate indoor environment concentrations of the hydroxyl radical ($1.23 \times 10^5\,\mathrm{molecules\,cm^{-3}}$) and ozone ($4.92 \times 10^{11}\,\mathrm{molecules\,cm^{-3}}$) have been previously estimated by Sarwar et al. (2002). Using the citronellol/OH and citronellol/O_3 rate constants reported here 1/e lifetimes of 0.075 and $0.42\,\mathrm{h^{-1}}$ were determined, respectively. Comparing these values to a typical indoor air exchange rate of $0.6\,\mathrm{h^{-1}}$, the citronellol/O_3 reaction is expected to be the most likely indoor environment loss mechanism for citronellol.

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