Limonene ozonolysis in the presence of nitric oxide: Gas-phase reaction products and yields

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HIGHLIGHTS

- Aqueous collection and derivatization of gas-phase limonene ozonolysis products.
- Multi-functional gas-phase carbonyls detected from limonene ozonolysis.
- Hydroxyl radical's and nitric oxide's influence on reaction product formation.

ARTICLE INFO

ABSTRACT

The reaction products from limonene ozonolysis were investigated using the new carbonyl derivatization agent, *O-tert*-butylhydroxylamine hydrochloride (TBOX). With ozone (O_3) as the limiting reagent, five carbonyl compounds were detected. The yields of the carbonyl compounds are discussed with and without the presence of a hydroxyl radical ($OH^•$) scavenger, giving insight into the influence secondary OH radicals have on limonene ozonolysis products. The observed reaction product yields for limona-ketone (LimaKet), 7-hydroxyl-6-oxo-3-(prop-1-en-2-yl)heptanal (7H6O), and 2-acetyl-5-oxohexanal (2A5O) were unchanged suggesting $OH^•$ generated by the limonene + O_3 reaction does not contribute to their formation. The molar yields of 3-isopropenyl-6-oxo-heptanal (IPOH) and 3-acetyl-6-oxoheptanal (3A6O) decreased by 68% and >95%; respectively, when $OH^•$ was removed. This suggests that $OH^•$ radicals significantly impact the formation of these products. Nitric oxide (NO) did not significantly affect the molar yields of limonaketone or IPOH. However, NO (20 ppb) considerably decreased the molar reaction product yields of 7H6O (62%), 2A5O (63%), and 3A6O (47%), suggesting NO reacted with peroxyl intermediates, generated during limonene ozonolysis, to form other carbonyls (not detected) or organic nitrates. These studies give insight into the transformation of limonene and its reaction products that can lead to indoor exposures.

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1. Introduction

Volatile organic compounds (VOCs) are introduced indoors by outdoor ventilation, emissions from building materials, and the use of various cleaning products (Nazaroff and Weschler, 2004; Singer et al., 2006). In indoor environments, these VOCs can react with oxidants such as ozone (O_3) and/or hydroxyl radicals ($OH^•$) in the gas phase or on indoor surfaces and can transform into a variety of intermediate and stable oxygenated organics (e.g. peroxyl radicals, aldehydes, ketones, di- and tricarbonyls, and carboxylic acids).

Peroxyl radicals may further react with NO or NO_2 to generate organic nitrates (e.g alkyl nitrates, peroxyacyl nitrates (PANs), hydroxynitrates, and dinitrates) (Finlayson-Pitts and Pitts, 2000). Indoor concentrations of O_3, NO, and NO_2 in the US have been measured with average values of 50, 50, and 25 ppb, respectively (Nazaroff and Cass, 1986; Weschler and Shields, 1997; Weschler et al., 1994). Although, hydroxyl radical concentrations have not been measured indoors, they have been estimated to be in the range of $0.12-2 \times 10^6$ mol cm^{-3} ($0.48-8 \times 10^{-5}$ ppb) (Alvarez et al., 2013; Sarwar et al., 2002; Waring and Wells, 2015).

Given these measured oxidant concentrations indoors and the reactivity of specific VOCs (e.g. terpenes such as α-pinene, limonene, terpinolene), it is expected that oxidation products are formed and lead to potential indoor exposures. As an example, the

bimolecular rate constant for terpinolene + O_3 is 19.0×10^{-16} cm^3 $molecule^{-1}$ s^{-1} (0.169 ppb^{-1} hr^{-1}) (Atkinson and Arey, 2003; Nazaroff and Weschler, 2004). Assuming an indoor O_3 concentration of 50 ppb, the pseudo-first order rate for terpinolene ozonolysis would be 8.45 hr^{-1} indicating terpinolene would likely be removed by reaction with O_3 before removal by a typical air-exchange of 0.6 hr^{-1} (Wilson et al., 1996). Therefore, identifying reaction products from terpene ozonolysis that occurs indoors is critical to characterizing occupant exposures.

Limonene (1-methyl-4-(prop-1-en-2-yl)cyclohexene), is a prevalent terpene with a strong orange-like fragrance found in a number of household consumer products used indoors. The National Library of Medicine's (NLM) Household Products Database (HHS/NIH, 2015) lists 166 consumer products that contain D-limonene as an ingredient. A significant fraction (59 of 166) of these products are used inside the home (e.g., in cleaning agents) which frequently use D-limonene as an odorant and for its antimicrobial properties. Recent work by Singer et al. determined the one hour concentration of limonene after the application of a full strength cleaning product to be 300−6000 $\mu g/m^3$ (~80−1600 ppb) (Singer et al., 2006).

The ozonolysis of limonene has been extensively studied using a variety of analytical techniques. However, most of this research has focused on the characterization of secondary organic aerosols (SOAs) from the formation of gas-phase species (Donahue et al., 2014; Ebben et al., 2012; Jiang et al., 2012; Pan et al., 2009; Pathak et al., 2012b; Youssefi and Waring, 2014). This research has provided information about the particle size distribution, aerosol yields and chemical composition, but only limited information of the gas-phase yields from limonene ozonolysis has been determined. Questions still remain on the carbon mass balance of limonene oxidation. The answers may be related to undetected highly oxygenated products (e.g. tricarbonyls). Reaction models (e.g. Master Chemical Mechanism) propose the formation of tri-carbonyl species from limonene ozonolysis (Carslaw, 2013; Jenkin et al., 2015; Norgaard et al., 2013; Pathak et al., 2012a). Recently, the tricarbonyl (3-acetyl-6-oxoheptanal (3A6O)) from limonene ozonolysis was detected using the new derivatization agent, TBOX (Wells and Ham, 2014).

In this study, limonene ozonolysis with and without addition of nitric oxide (NO) and cyclohexane (OH• scavenger) was investigated using a Teflon® impinger to capture and characterize gas-phase reaction products. Identification and quantification of the reaction products (i.e., aldehydes, ketones, and di- and tri-carbonyls) was made using O-tert-butylhydroxylamine hydrochloride (TBOX) to derivatize the carbonyl products (Wells and Ham, 2014). This method provides the sensitivity, ease of use, and applicability needed for detection of carbonyl compounds at expected indoor air concentrations.

2. Experimental methods

2.1. Chemicals and solvents

All compounds were used as received and had the following purities: from Sigma-Aldrich/Fluka (St. Louis, MO): O-tert-butylhydroxylamine hydrochloride (TBOX, 99%), limonene (97%), toluene (HPLC grade, 99+%), cyclohexane (HPLC grade, 99+%), cyclohexanone (98%), methylglyoxal (40 wt% in water), and glutaraldehyde (50 wt% in water). Methanol (HPLC grade, 99+%) was purchased from Fisher Scientific (Pittsburgh, PA). Water (DI H_2O) was distilled, deionized to a resistivity of 18 MΩ cm, and filtered using a Milli-Q® filter system (Billerica, MA). Helium (UHP grade), the carrier gas, was supplied by Butler Gas (McKees Rocks, PA) and used as received. Experiments were carried out at (297 ± 3)

K and 1 atm pressure. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) and molecular sieves (Drierite) to remove both moisture and organic contaminants. This treated dry air from the NIOSH facility flowed through a mass flow controller and into a humidifying chamber and was subsequently mixed with dry air to the pre-determined relative humidity (RH) of 50%. An 80 L Teflon® reaction chamber contained in a light-tight wooden box was filled through a heated syringe injection port facilitating the introduction of liquid reactants into the chamber. Background measurements of the NIOSH facility air showed concentrations of O_3, NO, and NO_2 at less than 1.0, 1.2, and 0.5 ppb, respectively. All reactant mixtures were generated by this system.

Ozone was produced by photolyzing air with a mercury pen lamp (Jelight, Irvine, CA) in a separate Teflon® chamber. Aliquots of this O_3/air mixture were added to the Teflon® reaction chamber using a gas-tight syringe. O_3 concentrations were measured using a Thermo Electron (Waltham, MA) UV photometric ozone analyzer Model 49C. Aliquots of NO were added to the reaction chamber from a 100 ppm tank (Butler Gas, McKees Rocks, PA) using a gas-tight syringe. NO and NO_2 concentrations were measured using a Thermo Electron (Waltham, MA) NOx analyzer Model 49i.

2.2. Methods

2.2.1. Calibration

Experiments to measure the gas-phase carbonyls (cyclohexanone, and glutaraldehyde, Table 1) used for calibration of the gas-phase reaction products formed from the reaction of limonene with O_3 were conducted with a previously described apparatus (Ham et al., 2015; Wells and Ham, 2014). A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok (Solon, OH) fitting attached to an 80 L Teflon®-film chamber. The chamber was filled with 50% relative humidity (RH) air (described above).
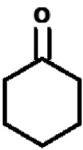
Calibration plots were made by analyzing triplicate measurements of standard solutions that were injected into an 80 L Teflon® chamber at 50% RH, ranging in concentration from 5 to 30 ppb (1.2−7.4 × 10^{11} mol cm^{-3}). Samples were obtained by pulling 60 L of air from the chamber using a pump (URG 3000-02Q, Chapel Hill, NC) into 25 mL of DI H_2O in a 60 mL Teflon® impinger (Savillex, Eden Prairie, MN). After collection, samples were decanted into 40 mL vials, then derivatized with 100 μL aqueous 250 mM TBOX, and placed in a heated water bath at 70 °C for 2 h. After removing the vial from the water bath and allowing to cool to room temperature, 0.5 mL of toluene was added to the vial. The vial was then shaken for 30 s and allowed to separate into a toluene layer and aqueous layer. Then 100 μL of the toluene layer was then removed with a pipette and placed in a 2 mL autosampler vial with a 100 μL glass insert (Resetk, Bellefonte, PA). Then 1 μL of the extract was analyzed by gas chromatography-mass spectrometry (GC/MS) (conditions described below).

2.2.2. Limonene + O_3 reactions

In an 80 L volume of air at 50% RH, O_3 (20−100 ppb; 0.5−2.5 × 10^{12} molecule cm^{-3}) was added to 1.7 ppm limonene (4.25 × 10^{13} molecule cm^{-3}), and allowed to react for 30 min. After the reaction, 60 L of sample was collected into 25 mL of deionized water using an impinger, TBOX derivatized, extracted, and analyzed (as described above). Additional experiments included the addition of cyclohexane (CH) to the reaction mixture to scavenge OH• formed from Criegee intermediates of limonene ozonolysis (Aschmann et al., 2002; Carslaw, 2013; Criegee, 1975; Forester and Wells, 2009). NO's effect on limonene ozonolysis with and without

Table 1
Compounds used for system calibration. Chromatographic retention time, structure and molecular weight and observed ions are listed.

RT (min.)	Structure (name)	Derivatized M.W.	EI ions (Rel.Intensity)
12.4	M.W. = 98 cyclohexanone	169	41(58), 57(85), 67(30), 81(40), 96(45), 114(100), 170(65)
20.5 20.7 21.0	M.W. = 100 glutaraldehyde	242	41(55), 57(95), 68(35), 99(35), 113(100), 130(50), 186(18), 242(5), 243(5)

OH• was also investigated. The results from each of these experiments are described below. Each experiment was done in duplicate.

All samples were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 μm film thickness) column and the following GC oven parameters: 40 °C for 2 min, then 5 °C min^{-1} to 200 °C, then 25 °C min^{-1} to 280 °C and held for 5 min. One μL of each sample was injected in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 130 °C for 2 min then 200 °C min^{-1} to 300 °C and held for 10 min. 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.

3. Results

3.1. Cyclohexanone, glutaraldehyde calibration

The two carbonyls cyclohexanone (surrogate for singly derivatized LimaKet) and glutaraldehyde (surrogate for doubly derivatized 7H6O, IPOH, 2A5O, and 3A6O), see Table 1) were used for the calibration of all limonene + O$_3$ reaction products, since standards of observed oxidation products were not readily available (Ham et al., 2015). The following retention times were observed: 12.4 min for singly derivatized cyclohexanone (MW = 169) and 20.5, 20.7, 21.0 min for doubly or triply derivatized glutaraldehyde (MW = 242). The limit of detection (determined from three times the standard deviation of the slope of the calibration curve for cyclohexanone and glutaraldehyde (all peaks summed) divided by the slope) for single and multi-carbonyls was 0.06, and 0.11 ppb, respectively.

Derivatization of nonsymmetric carbonyls using TBOX typically resulted in multiple chromatographic peaks due to stereoisomers of the oximes. Typically an M+1 ion was observed for the derivatized oxime compounds. 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. TBOX adds a mass of 71 to the molecular weight of each derivatized carbonyl. In most cases, the $m/z = 57$ ion relative intensity for the chromatographic peaks of the oximes was greater

than 50% in the mass spectrum. This ion was attributable to the t-butyl group (C$_4$H$_9^+$ fragment) and could be effectively used to generate selected ion chromatograms to identify derivatized carbonyl compounds in a mixture. All molar yields were determined from the total ion chromatograms.

3.2. Limonene ozonolysis: observed reaction products

The five main products: limonaketone (LimaKet), 7-hydroxy-6-oxo-3-(prop-1-en-2yl)heptanal (7H6O), 3-isopropenyl-6-oxo-heptanal (IPOH), 2-acetyl-5-oxohexanal (2A5O), and 3-acetyl-6-oxoheptanal (3A6O) from limonene ozonolysis are listed below and shown in Table 2. All limonene ozonolysis products are predicted using the Master Chemical Mechanism v. 3.3.1 (Jenkin et al., 2015). Specific product yields determined from plots (See Figures S1-S3) for the reactions: limonene + O$_3$, limonene + O$_3$ + cyclohexane, and limonene + O$_3$ + NO (20 ppb) are described below and results shown in Table 3. The errors reported in Table 3 were calculated by doubling the standard regression slope errors from the yield plots.

3.2.1. Retention time 18.5 min: 4-acetyl-1-methylcyclohexene (limonaketone)(LimaKet)

The chromatographic peak for the oxime observed at 18.5 min was observed as a reaction product of limonene + O$_3$ as seen in Fig. 1. The main ions (% relative peak height) are 41(10), 57(12), 65(17), 108(18), 121(19), 136(14), 153(12) and 209(17). If $m/z = 210$ is the M+1 ion, then a molecular weight of 138 (209−71 = 138) is expected for the carbonyl compound. Based on the ions observed, the proposed identity of this product is limonaketone (Hakola et al., 1994). The product yield determined using the cyclohexanone calibration curve as a surrogate was 0.0076 ± 0.0008 for limonene + O$_3$, 0.0081 ± 0.0009 for limonene + O$_3$ + CH, and 0.0052 ± 0.0005 for limonene + O$_3$ + NO (see Table 3). Gas-phase yields of limonaketone in this investigation are significantly lower than those reported by Hakola et al., 1994, who reported yields of 0.20 ± 0.03 for the OH reaction and ≤0.04 for the O$_3$ reaction using a GC-FID.

3.2.2. Retention time 23.7 and 24.1 min: 7-hydroxyl-6-oxo-3-(prop-1-en-2-yl)heptanal − (7H6O)

The chromatographic peaks for the oxime observed at 23.7 and

Table 2
Reaction products observed from limonene ozonolysis. Chromatographic retention time, structure and molecular weight and observed ions are listed.
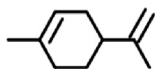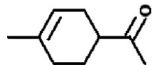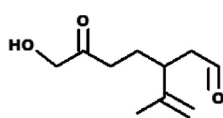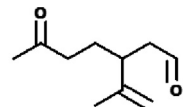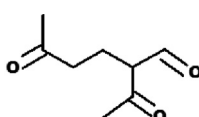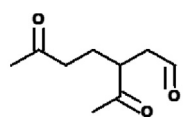
RT (min)	Structure (name)	Derivatized (MW)	EI ions (Rel.Intensity)
	 M.W. = 136 Limonene		
18.6	 M.W. = 138 Limonaketone (LimaKet)	208	41(10), 57 (12), 65(17), 108(18), 121(19), 136(14), 153(12), 209(17)
23.7 24.1	 M.W. = 184 7-hydroxyl-6-oxo-3-(prop-1-en-2yl)heptanal (7H6O)	255	41(40), 43(50), 57(80), 79(20), 107(55), 126(68), 139 (28), 182(18), 199(10), 256(1)
27.0 27.3 27.6	 M.W. = 168 3-isopropenyl-6-oxo-heptanal (IPOH)	310	41(50), 57(100), 73(28), 91(28), 107(34), 140(42), 166(40), 181(90), 198(60), 237(20), 254(30), 311(2)
29.3 29.6 29.9	 M.W. = 156 2-acetyl-5-oxohexanal (2A5O)	369	41(28), 57(48), 116(35), 125(25), 169(35), 172(15), 184(22), 240(22), 370(8)
31.5 31.7 31.9 32.0	 M.W. = 170 3-acetyl-6-oxoheptanal (3A6O)	383	41(15), 57(25), 65(17), 94(10), 165(25), 183(15), 198(17), 254(16), 310(15), 384(2)

Table 3
Molar yields of reaction products from limonene ozonolysis under different experimental conditions. CH = cyclohexane (OH$^{\bullet}$ radical scavenger).

Experiment	Molar yields				
	LimaKet	7H6O	IPOH	2A5O	3A6O
Limonene + O_3	0.0076 ± 0.0008	0.021 ± 0.001	0.160 ± 0.005	0.019 ± 0.003	0.015 ± 0.002
Limonene + O_3 + CH	0.0081 ± 0.0009	0.019 ± 0.003	0.050 ± 0.008	0.016 ± 0.003	X
Limonene + O_3 (20 ppb NO)	0.0052 ± 0.0005	0.008[a]	0.11 ± 0.01	0.007[a]	0.008[a]

X − Indicates 3A6O was only observed in the Limonene + O_3 (100 ppb) + CH experiment, no yield was measured.

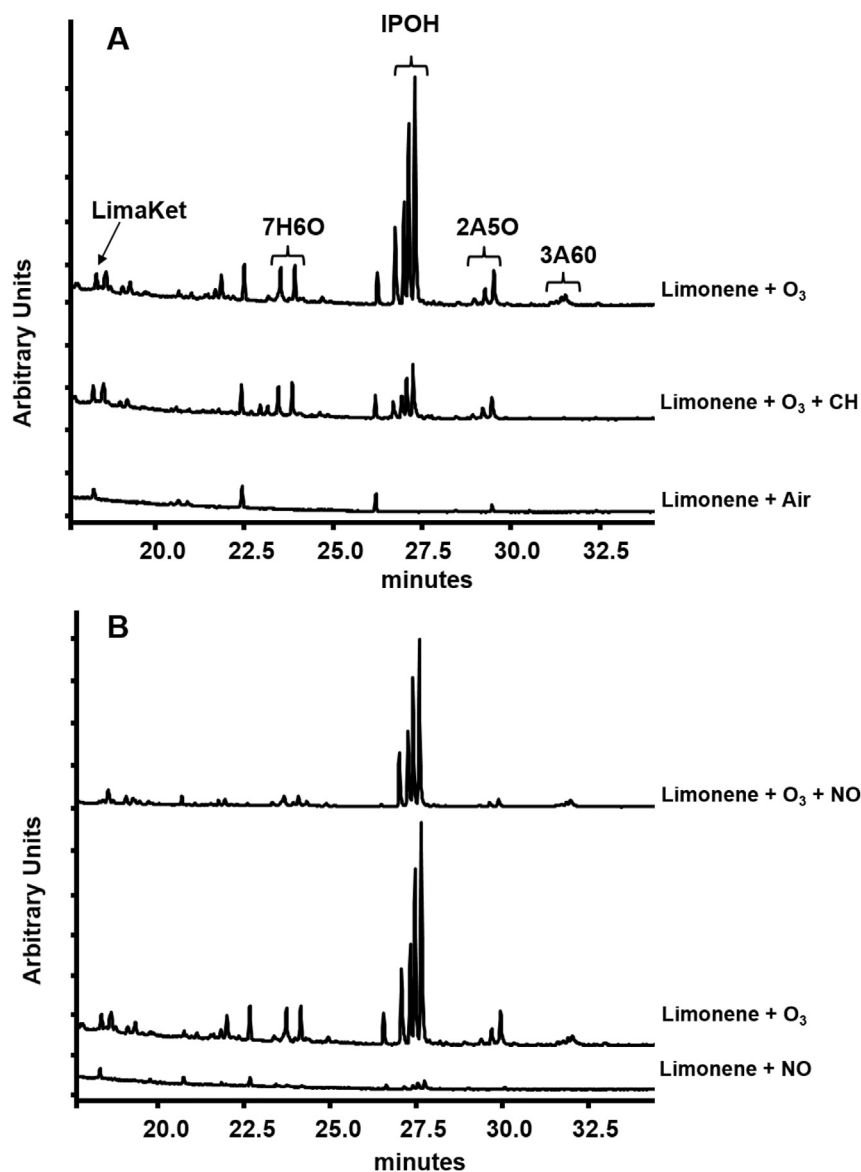[a] Indicates yields based on data from 100 to 50 ppb O_3 only just trace amounts of products were observed at 30 ppb O_3.

Fig. 1. Chromatograms from limonene ozonolysis with and without the addition of NO. (**A**) With and without addition of cyclohexane (OH• scavenger). (**B**) With and without addition of nitric oxide (NO).

24.1 min were observed as a reaction product of limonene + O_3 as seen in Fig. 1. The main ions (% relative peak height) are 41(40), 43(50) 57(80), 79(20), 107(55), 126(68), 139 (28), 182(18), 199(10), 256(1). If $m/z = 256$ is the M+1 ion, then a molecular weight of 184 ($255 - 71 = 184$) is expected for the carbonyl compound. Based on the ions observed, the proposed identity of this product is 7-hydroxyl-6-oxo-3-(prop-1-en-2-yl)heptanal. The product yield determined using the glutaraldehyde calibration curve as a surrogate was 0.021 ± 0.001 for limonene + O_3, 0.019 ± 0.003 for limonene + O_3 + CH, and 0.008 for limonene + O_3 + NO (see Table 3).

3.2.3. Retention time 27.0, 27.3, 27.4 and 27.6 min: 3-isopropenyl-6-oxo-heptanal − (IPOH)

The chromatographic peaks for the oxime observed at 27.0, 27.3, 27.4 and 27.6 min was observed as a reaction product of limonene + O_3 as seen in Fig. 1. The main ions (% relative peak height) are 41(50), 57(100), 73(28), 91(28), 107(34), 140(42), 166(40), 181(90), 198(60), 237(20), 254(30), 311(2). If $m/z = 311$ is

the M+1 ion, then a molecular weight of 168 ($310 - 71 - 71 = 168$) is expected for a dicarbonyl compound. Based on the ions observed, the proposed identity of this product is 3-isopropenyl-6-heptanal (IPOH). Further confirmation of this product was made from previous gas-phase limonene + O_3 studies (Hakola et al., 1994; Wells and Ham, 2014). The product yield determined using the glutaraldehyde calibration curve as a surrogate was 0.160 ± 0.005 for limonene + O_3, 0.050 ± 0.008 for limonene + O_3 + CH, and 0.11 ± 0.01 for limonene + O_3 + NO (see Table 3). Gas-phase yields of IPOH in this investigation are higher than in previous studies. Investigations of limonene + O_3 by Clausen et al. reported IPOH yields of 2–4% using GC-FID detection and Forester and Wells reported IPOH yields of 0.4% using GC/MS with PFBHA derivatization (Clausen et al., 2001; Forester and Wells, 2011).

3.2.4. Retention time 29.3, 29.6, 29.9 min: 2-acetyl-5-oxohexanal - (2A5O)

The chromatographic peaks for the oxime observed at 29.3, 29.6, and 29.9 min was observed as a reaction product of
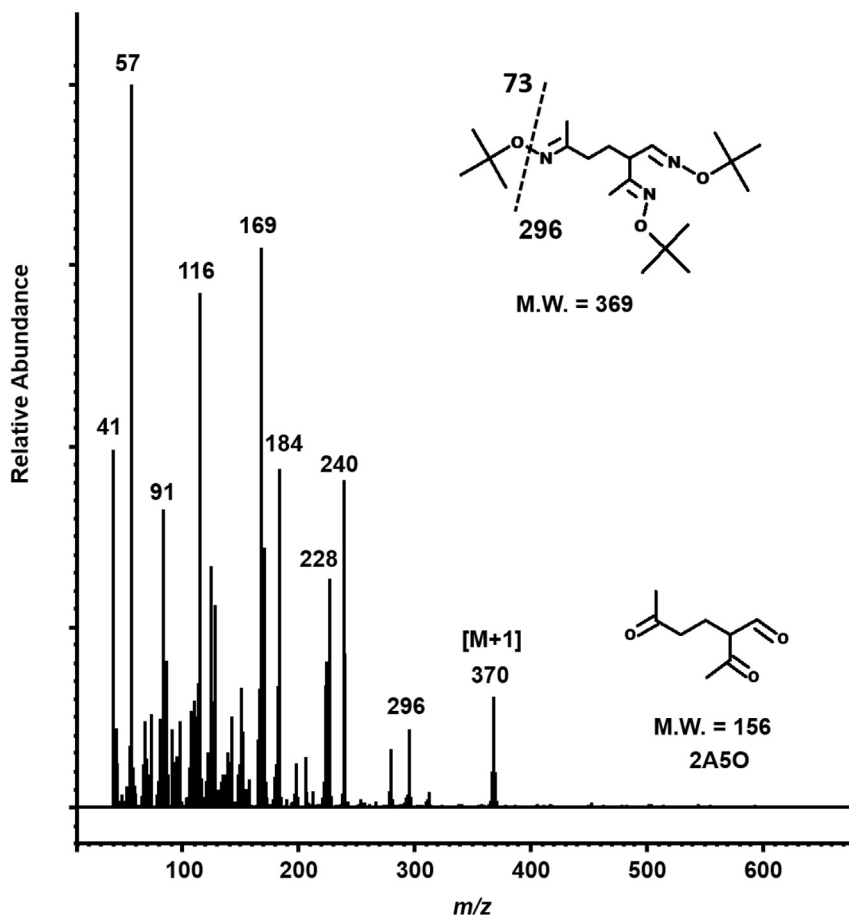
Fig. 2. Mass spectrum of 2-acetyl-5-oxohexanal (2A5O).

limonene + O$_3$ as seen in Fig. 1. The main ions (% relative peak height) are 41(28), 57(48), 116(35), 125(25), 169(35), 172(15), 184(22), 240(22), 370(8), see Fig. 2. If $m/z = 370$ is the M+1 ion, then a molecular weight of 156 ($369-71-71-71 = 156$) is expected for a tricarbonyl compound. Based on the ions observed, the proposed identity of this product is 2-acetyl-5-oxohexanal. The product yield determined using the glutaraldehyde calibration curve as a surrogate was 0.019 ± 0.003 for limonene + O$_3$, 0.016 ± 0.003 for limonene + O$_3$ + CH, and 0.007 for limonene + O$_3$ + NO (see Table 3). This oxidation product has not been observed previously.

3.2.5. Retention time 31.5, 31.7, 31.9 and 32.0 min: 3-acetyl-6-oxoheptanal − (3A6O)

The chromatographic peaks for the oxime observed at 31.5, 31.7, 31.9 and 32.0 min was observed as a reaction product of limonene + O$_3$ as seen in Fig. 1. The main ions (% relative peak height) are 41(15), 57(25), 65(17), 94(10), 165(25), 183(15), 198(17), 254(16), 310(15), 384(2). If $m/z = 384$ is the M+1 ion, then a molecular weight of 170 ($383-71-71-71 = 170$) is expected for a tricarbonyl compound. Based on the ions observed, the proposed identity of this product is 3-acetyl-6-oxoheptanal (Wells and Ham, 2014). The product yield determined using the glutaraldehyde calibration curve as a surrogate was 0.015 ± 0.002 for limonene + O$_3$ and 0.008 for limonene + O$_3$ + NO. (see Table 3). This product was not observed in the limonene + O$_3$ + CH experiments.

4. Discussion

As stated earlier, the ozonolysis of limonene has been extensively studied using a variety of analytical techniques (Hakola et al., 1994; Larsen et al., 2001; Leungsakul et al., 2005; Wells and Ham, 2014). Ozone can react with limonene via addition to either the endocyclic or exocyclic carbon-carbon double bonds with calculated rate constants (AOPWIN v.1.92a) of 43 and 1.2×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively (EPA, 2000). These numbers suggest that the endocyclic O$_3$ addition is favored by about 35 to 1 over the exocyclic O$_3$ addition.

When O$_3$ adds to either of these double bonds, a primary ozonide is formed which subsequently decomposes to a Criegee intermediate (Aschmann et al., 2002; Atkinson et al., 1992; Criegee, 1975; Forester and Wells, 2011). Further unimolecular decay of the Criegee intermediate may then lead to formation of OH• which can further react with excess limonene or newly formed reaction products. The OH• yield from ozonolysis of limonene has been reported to be 64–80% (Aschmann et al., 2002; Forester and Wells, 2009; Herrmann et al., 2010). The OH• can add to double bonds (similarly to O$_3$) and/or abstract available hydrogens leading to product formation. The calculated OH• rate constants for reaction with limonene from the endocyclic double bond and the exocyclic double bond obtained from AOPWIN are (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) 86.9 and 51.4, respectively. To determine which oxidation products were formed via ozonolysis alone and/or a combination of OH• and O$_3$, the hydroxyl radical scavenger (cyclohexane) was added to the system. The effect of OH• on the formation of each product is described below.
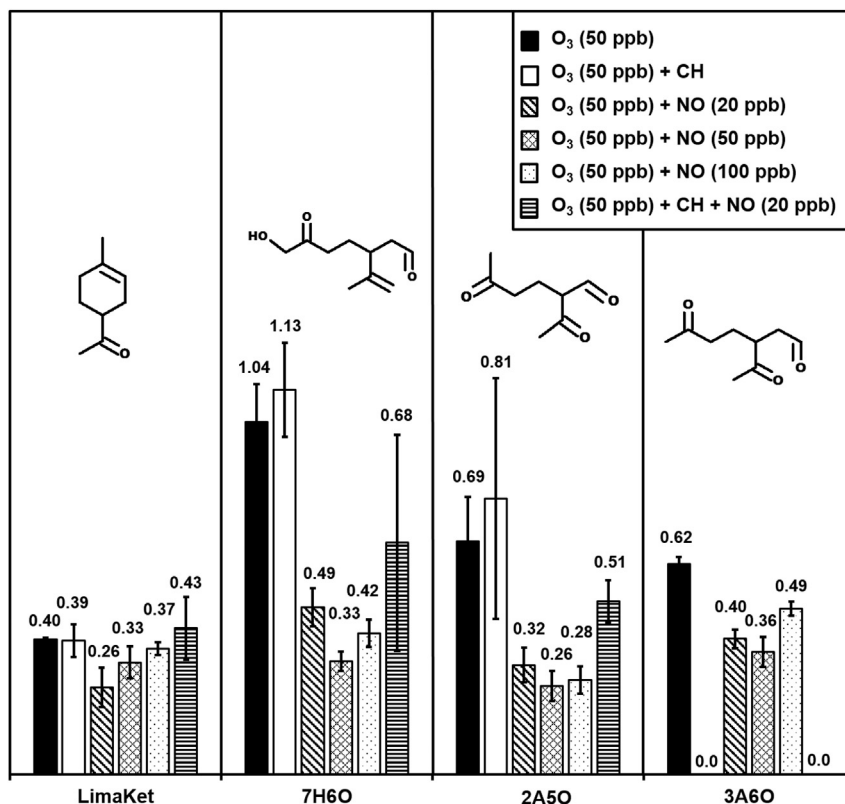
Fig. 3. Concentrations of observed reaction products after addition of NO and cyclohexane (CH) to scavenge OH radicals. IPOH has been omitted from figure for clarity.

4.1. Limonene + O₃ and OH• reaction products and yields

Previous investigations of limonene ozonolysis have reported two of the reaction products (LimaKet, IPOH) shown in the current investigation (Clausen et al., 2001; Forester and Wells, 2011; Hakola et al., 1994). Moreover, use of TBOX as the derivatization agent has afforded the observance of three additional oxidation products that have been predicted through models such as the MCM. A proposed reaction mechanism based on the data is described below.

LimaKet, 7H6O, and 2A5O are primary oxidation products formed only from the limonene + O₃ reaction, and not from secondary OH• formation as observed in Fig. 3 and Table 3. When OH• are scavenged, no statistically significant effects (7, 10, and 15% change, respectively) based on molar yields were observed, indicating that OH• is not influential in their formation. However, the formations of IPOH and 3A6O were strongly dependent on the presence of OH•. When OH• was scavenged, the molar yields decreased by 68% and >95%, respectively. This data further emphasizes the importance of OH• chemistry and how it strongly influences indoor reactions.

The mechanisms for the formation of LimaKet, IPOH, and 3A6O from limonene ozonolysis have been previously discussed (Carslaw, 2013; Lee et al., 2006; Wells and Ham, 2014). A mechanism for their formation can be found in the Supplementary Information, Figure S4. The ozonolysis product, 7H6O, is likely formed via ozone addition to the endocyclic carbon-carbon double bond, formation of a primary ozonide, and then subsequent cleavage to form the radical LIMOOA, as seen in the MCM. Subsequent decomposition of LIMOOA leads to the dicarbonyl peroxyl radical (LIMALBO2) which reacts with an alkoxyl radical to form the stable oxidation product, 7H6O.

The ozonolysis product, 2A5O, can be formed through multiple

mechanisms as detailed in the MCM v.3.3.1. One mechanism (Figure S4) may involve initial ozone addition to the exocyclic double bond to form LimaKet, as previously described (Hakola et al., 1994; Wells and Ham, 2014). Subsequent, ozone addition to the endocyclic double bond of LimaKet, followed by cleavage of the primary ozonide, leads to the radical CH₃C(=O)CH₂CH₂CH(C(=O)CH₃)CH₂·(OO•)H. The reaction then likely proceeds via hydrogen abstraction of the adjacent CH₂ and decomposition to form CH₃C(=O)CH₂CH₂CH(C(=O)CH₃)CH₂• and CH₂·OOH. The larger radical adds O₂ and stabilizes to form the tricarbonyl, 2A5O. Although this proposed mechanism does explain the formation of 2A5O through plausible steps, secondary addition of ozone to LimaKet seems unlikely due to the low concentration of ozone used in these experiments. Alternatively, it is possible that the reaction proceeds through initial O₃ addition to the endocyclic bond of limonene to form an intermediate similar to IPOH. This intermediate then reacts with another O₃ molecule to form the tricarbonyl. While the mechanism for 2A5O is not clear, the observation of this product highlights the formation of tricarbonyl species.

4.2. Nitric oxide (NO) effect

When NO is added to the limonene + O₃ reaction system, there are several pathways for NO to affect the reaction system. NO can react with O₃ leading to NO₂ with a rate constant of $k_{O3+NO} = 2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (Wallace et al., 1980). NO can also react with peroxyl radicals (RO₂•) generated from OH• and/or O₃ reactions to form stabilized carbonyls and/or organic nitrates (Finlayson-Pitts and Pitts, 2000). These reactions are typically fast with a rate constant of $k_{RO2•+NO} = 7 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Finlayson-Pitts and Pitts, 2000).

Addition of NO (20, 50, and 100 ppb) to the limonene + O₃

(50 ppb) system had no statistical effect in the formation of LimaKet or IPOH, Fig. 3. However, when NO is held constant (20 ppb) and O_3 was increased (30, 50, and 100 ppb), the molar yields of both LimaKet and IPOH decreased by 31.6% and 31.2%, respectively (Table 3). As O_3 was increased, the ratio of $RO_2^•$/NO also increased which affected the rate of the $RO_2^•$ + NO reaction leading to the formation of organic nitrates. The addition of NO had a more significant effect on 7H6O, 2A5O, and 3A6O. A decrease in their formation was observed with the addition of NO (20, 50, and 100 ppb) to the limonene + O_3 (50 ppb) system, Fig. 3. Furthermore, when NO is held constant (20 ppb) and O_3 was increased (30, 50, and 100 ppb), the molar yields of 7H6O, 2A5O, and 3A6O decreased by 61.9%, 63.3%, and 46.7%, respectively, Table 3. This suggests that peroxyl radical intermediates likely react with NO to form organic nitrates.

Interestingly, 7H6O and 2A5O (Fig. 3) increase when cyclohexane is added in the presence of NO. This may be explained by the side reaction of NO with cyclohexylperoxyl ($CHRO_2^•$) radicals. When OH• is scavenged by cyclohexane, CH• can be formed, which then reacts in a diffusion-controlled manner with O_2 to form $CHO_2^•$ (Finlayson-Pitts and Pitts, 2000; Neuenschwander et al., 2010). These $CHO_2^•$ effectively out-compete $RO_2^•$ that form 7H6O and 2A5O for reaction with NO, resulting in higher yields of these two products.

5. Conclusion

Limonene ozonolysis with and without addition of NO and cyclohexane (OH• scavenger) was studied using the new derivatization agent, O-tertbutylhydroxylamine hydrochloride (TBOX). The molar yields of the observed single, di- and tricarbonyl reaction products (LimaKet, 76HO, IPOH, 2A5O, and 3A6O) from limonene + O_3, limonene + O_3 + cyclohexane, and limonene + O_3 + NO experiments were also determined. The scavenging of secondary OH• reduced the yields of IPOH and 3A6O highlighting the significance of OH•'s role in the overall limonene oxidation. In the presence of NO, the molar yields for LimaKet and IPOH were not significantly affected; however, the yields of 7H6O, 2A5O, and 3A6O were reduced by > 45% suggesting other possible routes in forming undetected carbonyls or organic nitrates. These studies further highlight the importance NO has on the formation of oxidation products in the gas phase. Future investigations will include the addition of NO_2 to study its effect on the ozonolysis of both single and mixtures of terpenes.

Disclaimer

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.03.003.

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