

Appendix I

Gas-Phase Products and Secondary Aerosol Yields from the Ozonolysis of Ten Different Terpenes^{*}

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Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes

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[1] The ozonolyses of six monoterpenes (α -pinene, β -pinene, 3-carene, terpinolene, α -terpinene, and myrcene), two sesquiterpenes (α -humulene and β -caryophyllene), and two oxygenated terpenes (methyl chavicol and linalool) were conducted individually in Teflon chambers to examine the gas-phase oxidation product and secondary organic aerosol (SOA) yields from these reactions. Particle size distribution and number concentration were monitored and allowed for the calculation of the SOA yield from each experiment, which ranged from 1 to 54%. A proton transfer reaction mass spectrometer (PTR-MS) was used to monitor the evolution of gas-phase products, identified by their mass to charge ratio (m/z). Several gas-phase oxidation products, formaldehyde, acetaldehyde, formic acid, acetone, acetic acid, and nopinone, were identified and calibrated. Aerosol yields, and the yields of these identified and calibrated oxidation products, as well as many higher m/z oxidation products observed with the PTR-MS, varied significantly between the different parent terpene compounds. The sum of measured oxidation products in the gas and particle phase ranged from 33 to 77% of the carbon in the reacted terpenes, suggesting there are still unmeasured products from these reactions. The observations of the higher molecular weight oxidation product ions provide evidence of previously unreported compounds and their temporal evolution in the smog chamber from multistep oxidation processes. Many of the observed ions, including m/z 111 and 113, have also been observed in ambient air above a Ponderosa pine forest canopy, and our results confirm they are consistent with products from terpene + O₃ reactions. Many of these products are stable on the timescale of our experiments and can therefore be monitored in field campaigns as evidence for ozone oxidative chemistry.

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1. Introduction

[2] Biogenic emissions of terpene compounds influence atmospheric chemistry through the formation of tropospheric ozone and the production of secondary organic aerosol (SOA). Terpenes encompass several wide classes of compounds, including monoterpenes (C₁₀H₁₆), sesquiterpenes (C₁₅H₂₄), and oxygenated terpenes (e.g., C₁₀H₁₈O, C₁₀H₁₂O). These compounds are emitted from conifers as well as broad-leaved trees as a function of temperature, or both temperature and light [Kesselmeier and Staudt, 1999]. They react with OH, O₃, and NO₃, the common atmo-

spheric oxidants, with lifetimes that range from minutes to days [Atkinson and Arey, 2003]. Several monoterpene oxidation products are known to undergo gas-particle partitioning and have been found in ambient air in the gas and particle phases [Yu *et al.*, 1999b], [Kavouras *et al.*, 1999].

[3] Experiments examining terpene oxidation have been conducted after F. W. Went first suggested that blue hazes in forested regions were products of these reactions [Went, 1960]. Early experiments determined rate constants for the reaction of many different terpenes with the major atmospheric oxidants [e.g., Atkinson *et al.*, 1990; Shu and Atkinson, 1995], and yields of SOA and gas-phase carbonyl products from the oxidation of common monoterpene species, such as α - and β -pinene [e.g., Hatakeyama *et al.*, 1989; Pandis *et al.*, 1991; Zhang *et al.*, 1992; Hakola *et al.*, 1994]. Studies on the yields of OH from the ozonolysis of terpenes and other alkenes, from the decomposition of activated carbonyl oxides, or Criegee intermediates (CI), have also been conducted and found to occur at atmospheric

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pressure, with yields, for some terpenes, near unity [e.g., Atkinson *et al.*, 1992; Kroll *et al.*, 2001; Aschmann *et al.*, 2002]. Thus, for ozonolysis experiments, an OH scavenger is often added to the chamber to avoid the confounding effects of simultaneous O₃ and OH oxidation reactions. Recent work has suggested that the choice of OH scavenger influences SOA yield in alkene ozonolysis [Docherty and Ziemann, 2003; Keywood *et al.*, 2004a]. Keywood *et al.* [2004a] determined that the main influence of the scavenger results from the production of HO₂ radicals, altering the HO₂/RO₂ ratio, with higher ratios (ratio from CO > 2-butanol > cyclohexane) resulting in enhanced SOA production. Additionally, the structure of the parent compound, e.g., cyclic or acyclic, determined the sensitivity of SOA yield to the type of OH scavenger used [Jenkin, 2004; Keywood *et al.*, 2004a]. Recently, the predominance of organic peroxides found in monoterpene-generated SOA provided evidence for oligomer formation from heterogeneous reactions between hydroperoxides and aldehydes [Docherty *et al.*, 2005], catalyzed by the acidic component of the aerosol phase [Jang *et al.*, 2002].

[4] Ambient air temperature is known to affect the partitioning of semivolatile oxidation products between the gas and particle phases. Relative humidity has also been shown to affect the yields of nopinone and pinonaldehyde from β -pinene and α -pinene, respectively. The reaction between water and the stabilized C₉-CI resulted in additional formation of nopinone [Winterhalter *et al.*, 1999] or pinonaldehyde [Baker *et al.*, 2001; Warscheid and Hoffmann, 2001], with SOA yields doubling from dry to humid conditions. Additionally, Baker *et al.* [2001] found that the pinonaldehyde formation yield was independent of RH over a range of ~5–50%, suggesting that the Criegee intermediates react dominantly with water, even at relatively low RH values. Numerous other gas-phase oxidation products have been identified from the ozonolysis of terpenes, including low molecular weight products, e.g., formaldehyde, acetone, and formic acid, and higher molecular weight products that are often specific to the parent terpene, such as nopinone and pinonaldehyde, mentioned above, as well as other multifunctional compounds with carbonyl, carboxyl, or hydroxyl groups [e.g., Calogirou *et al.*, 1999, and references therein; Yu *et al.*, 1999a; Jang and Kamens, 1999].

[5] Recent field studies have provided observational support that terpenes can be oxidized within a forest canopy before detection by above-canopy flux techniques. In an orange grove in Spain, β -caryophyllene, a reactive sesquiterpene, was observed in branch enclosures but not in simultaneous measurements above the canopy, suggesting that β -caryophyllene was oxidized within the canopy [Ciccioli *et al.*, 1999]. In a California Ponderosa pine forest, chemical O₃ flux to the ecosystem scaled exponentially with temperature in a similar manner as monoterpenes [Kurpius and Goldstein, 2003], and from the same site, elevated monoterpene fluxes to the atmosphere from the mastication of Ponderosa pine trees [Schade and Goldstein, 2003] resulted in increased chemical O₃ flux to the ecosystem [Goldstein *et al.*, 2004], suggesting a linkage between chemical ozone loss in the canopy and terpene emissions. In subsequent work, Holzinger *et al.* [2005] observed large quantities of previously unmeasured

oxidation products above the same Ponderosa pine forest canopy. In a northern Michigan forest, elevated nighttime OH concentrations correlated with O₃ mixing ratios, suggesting that OH was produced from reactions between O₃ and unmeasured terpenes [Faloona *et al.*, 2001]. From the same forest, higher than expected OH reactivity was observed and scaled exponentially with temperature in a similar manner as biogenic emissions [Di Carlo *et al.*, 2004]. Taken together, these results provide convincing evidence of chemical loss of reactive compounds within the forest canopy through oxidation by OH and O₃.

[6] Here, we report the results from a series of chamber experiments conducted in March and April of 2003, examining the gas-phase oxidation products and gas and particle-phase yields obtained from terpene + O₃ reactions, in the presence of an OH scavenger and ammonium sulfate seed aerosol. The suite of terpene compounds used in these experiments is representative of emissions from Ponderosa pine trees [e.g., Lee *et al.*, 2005] and other terpene-emitting vegetation, [e.g., Kesselmeier and Staudt, 1999; Fuentes *et al.*, 2000; Geron *et al.*, 2000, and references therein]. We focus primarily on the time evolution and yields of gas-phase oxidation products, and propose structures and partial formation mechanisms for many of the observed products from myrcene, terpinolene, and α -terpinene. The gas-phase oxidation products observed from terpene + O₃ experiments, identified by their mass to charge ratio (*m/z*), provided a guide to the interpretation of the oxidation product masses observed in and above the Ponderosa pine forest canopy by PTR-MS [Holzinger *et al.*, 2005]. Additionally, the molar yields of the low molecular weight gas-phase oxidation products, such as formaldehyde, acetaldehyde, formic acid, acetone, and acetic acid, are useful for understanding and modeling the impacts of terpene emissions to the atmosphere. The high variability in yield of gas-phase oxidation products and SOA between the different terpene compounds tested highlights the variable impacts of the different terpenes on regional atmospheric chemistry and suggests that this species variability should be accounted for in models of gas and particle-phase products from terpene oxidation.

2. Experiment

[7] The ozonolysis experiments were conducted at the Caltech Indoor Chamber Facility, which has been described in detail elsewhere [Cocker *et al.*, 2001; Keywood *et al.*, 2004b]. Briefly, the facility consists of two suspended 28 m³ flexible Teflon chambers that maintain atmospheric pressure at all times. Temperature and relative humidity (RH) inside the chamber were measured using combined temperature and RH probes (Vaisala HMP233 series transmitters, Woburn, Massachusetts). The accuracy of the probe is 0.001°C and 2% RH, when calibrated against salt solutions. Experiments were conducted at 20 ± 1°C and <10% RH with a drift within 5% (see Table 2 in section 3.1). O₃ concentrations were measured using an ambient O₃ monitor (Horiba APOA-360, Irvine, California), and calibrated using an internal O₃ generator and N₂ as zero air. The uncertainty in the O₃ measurement was ±3%. These experiments were conducted under low NO_x conditions, with concentrations <5 ppb.

Compound	Structure	Formula	m/z	k_{ozone} ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)	Description
3-carene		$\text{C}_{10}\text{H}_{16}$	137	3.7×10^{-17}	bicyclic, internal double bond
α -terpinene		$\text{C}_{10}\text{H}_{16}$	137	2.1×10^{-14}	monocyclic, 2 internal double bonds
β -caryophyllene		$\text{C}_{15}\text{H}_{24}$	205	1.16×10^{-14}	bicyclic, 1 internal, 1 external double bond
α -humulene		$\text{C}_{15}\text{H}_{24}$	205	1.17×10^{-14}	monocyclic, 3 internal double bonds
α -pinene		$\text{C}_{10}\text{H}_{16}$	137	8.4×10^{-17}	bicyclic, internal double bond
terpinolene		$\text{C}_{10}\text{H}_{16}$	137	1.9×10^{-15}	monocyclic, 1 internal, 1 external double bond
β -pinene		$\text{C}_{10}\text{H}_{16}$	137	1.5×10^{-17}	bicyclic, 1 external double bond
myrcene		$\text{C}_{10}\text{H}_{16}$	137	4.7×10^{-16}	acyclic, 3 double bonds
methyl chavicol		$\text{C}_{10}\text{H}_{12}\text{O}$	149		aromatic, oxygenated, 1 external double bond
linalool		$\text{C}_{10}\text{H}_{18}\text{O}$	155		acyclic, oxygenated, 2 double bonds

Figure 1. Parent terpene compounds used in the experiments, listed in order of decreasing aerosol production. Rate constants were obtained from *Atkinson and Arey* [2003, and references therein].

[8] Particle size distribution and number concentration were measured separately from each chamber using two cylindrical scanning electrical mobility spectrometers. Particle phase instrumentation and calibration, and generation of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, seed aerosol are described in more detail elsewhere [Keywood *et al.*, 2004b]. The presence of seed aerosol generally suppressed nucleation, and acted as a surface for the condensation of oxidation products, contributing to the measured yield of

secondary organic aerosol. The initial volume of the aerosol was accurately known as the seed aerosol was intentionally prepared within the measurement size range of the SEMS. The starting concentration of seed aerosol was about 20,000 particles cm^{-3} , with a mean diameter of 80–100 nm.

[9] Ten different terpene compounds were reacted in these experiments: six monoterpenes (α -pinene, β -pinene, 3-carene, terpinolene, α -terpinene, and myrcene), two sesquiterpenes (α -humulene and β -caryophyllene), and two

oxygenated terpenes (methyl chavicol, also known as 4-allylanisole, and linalool). Figure 1 lists the structures and m/z of the parent terpenes used and the rate constants for their reactions with ozone (k_{ozone}). Gas-phase concentrations of the parent terpene were monitored using two instruments: a Hewlett Packard gas chromatograph with a flame ionization detector (GC-FID) using a 60 m $\times$ 0.32 μm DB-5 column (J&W Scientific, Davis, California), and a proton transfer reaction mass spectrometer, or PTR-MS (Ionicon Analytik, Innsbruck, Austria) [Lindinger *et al.*, 1998]. Air from the reaction chamber was sampled using SilcoSteel (Restek Corporation, Bellefonte, Pennsylvania) tubing, and pulled through a 2 μm pore size PTFE particulate filter (Pall Corporation, East Hills, New York) before analysis by PTR-MS, which measured parent terpenes as well as gas-phase oxidation products. The PTR-MS is a quadrupole mass spectrometer that uses hydronium ions (H_3O^+) to chemically ionize the compound of interest through a proton transfer reaction. Thus any compound that has a proton affinity higher than that of water can be detected by the PTR-MS, and is identified by its mass to charge ratio (m/z). Because compounds are identified by their molecular weight plus 1 (H^+), the PTR-MS is unable to distinguish between different compounds with the same molecular weight. However, because of the controlled nature of these laboratory chamber experiments, where one terpene at a time is reacted with O_3 , increasing count rates of certain ions are indicative of oxidation products from these reactions. Knowledge of the structures of the parent terpene allows for the deduction of possible identities of the oxidation products from reasonable oxidation mechanisms. However, structurally different oxidation products that have the same mass cannot be distinguished from one another by PTR-MS.

[10] Microliter volumes of individual liquid monoterpenes and oxygenated terpenes were injected into a 250 mL glass bulb and gently heated as a stream of clean air passed through the bulb, vaporizing the terpene and carrying it into the chamber. Cyclohexane was injected in the same way. Because of their high boiling points ($>250^\circ\text{C}$), liquid sesquiterpenes were injected with cyclohexane simultaneously, using the cyclohexane as a carrier for the sesquiterpenes. The starting concentration of the parent hydrocarbon was measured by GC-FID and PTR-MS (monoterpenes), or by PTR-MS (sesquiterpenes and oxygenated terpenes), and was allowed to stabilize before the injection of O_3 initialized the reaction. O_3 was generated using a UV lamp ozone generator (EnMet Corporation, Michigan) and was injected into the chamber at 5 L min^{-1} . The total concentration of O_3 was sufficient to exceed the parent terpene concentration by at least a factor of 3 in each experiment.

2.1. Gas-Phase Measurements and Calibrations

[11] For calibrations, each pure terpene compound was diluted in cyclohexane and injected into a Teflon bag filled to a final volume of 50 L. All parent terpene compounds were obtained from Fluka Chemicals through Sigma-Aldrich (St. Louis, Missouri). The monoterpenes were calibrated from the same Teflon bag simultaneously by GC-FID and PTR-MS, and the sesquiterpenes and oxygenated terpenes were only calibrated using PTR-MS. Calibra-

tion curves were generated from measurements at three different terpene concentrations. The five low molecular weight oxidation products: formaldehyde, acetaldehyde, formic acid, acetone, and acetic acid, and two higher molecular weight oxidation products, nopinone, from β -pinene oxidation, and α -pinene oxide, from α -pinene oxidation, were also calibrated in the PTR-MS using Teflon bags. Nopinone was diluted in cyclohexane before injection into the bag, and the other five oxidation products were diluted in ultrapure water prepared by the Millipore Milli-Q system (Billerica, Massachusetts). Two different Teflon bags were used for the calibrations to separate cyclohexane-based and water-based solutions. The standard error of the slope of the calibration curves for all terpene compounds and (calibrated) oxidation products was $<3\%$, except for α -humulene (standard error $\sim 7\%$), and acetaldehyde (standard error $\sim 4\%$). Additional sources of error include the accuracies of the syringe, the volumetric flask used for the terpene dilutions, and the flow controller, together contributing an uncertainty of 3–5%.

[12] The concentrations of compounds for which pure commercial standards were not available were estimated on the basis of the rate constant (k) of the proton transfer reaction, according to the equation [Lindinger *et al.*, 1998]:

$$[R] = \frac{[RH^+]}{[H_3O^+]_0 kt} \quad (1)$$

where $[R]$ is the unknown concentration of the compound of interest, and $[RH^+]$ is the signal of the protonated compound, $[H_3O^+]$ is the primary ion signal, and t is the reaction time in the drift tube. Because the proton transfer reaction rate constants are not known for all compounds, an estimated rate constant (k) of $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used for those compounds without a measured rate constant. The rate constants for the proton transfer reaction of most compounds are generally within $\pm 20\%$ of the estimated k .

[13] Between experiments, the chambers were continuously flushed with clean compressed air that passed through four scrubbing cartridges containing activated carbon, silica gel, Purafil, and molecular sieves, respectively, and a HEPA filter before entering the Teflon chambers. The chambers were flushed for 36 h before the start of an experiment, which reduced O_3 and particle concentrations to below 1 ppb and 100 particles cm^{-3} , respectively. Hydrocarbon concentrations inside the chamber, before the injection of the terpene, were below detection limit for all parent terpenes. Higher background counts from the blank chamber air were observed for the low molecular weight oxidation products, resulting in higher detection limits for those compounds. The detection limit ($1\sigma_{\text{background counts/sensitivity}}$) for the terpenes was <70 ppt, for nopinone: 20 ppt, for acetaldehyde and acetone: <1 ppb, for formic acid and acetic acid: <2 ppb, and for formaldehyde: 4 ppb. Starting concentrations for formaldehyde and formic acid, m/z 31 and 47, respectively, were <10 ppb, calculated from count rate divided by the sensitivity of the PTR-MS to those compounds. The background count rate on m/z 31 does not result from formaldehyde, but rather from interference from other ions, such as the ^{15}N isotope of NO^+ . Additionally, back reactions between protonated formaldehyde

(CH₂OH⁺) and H₂O make PTR-MS measurements of formaldehyde in ambient air difficult because of low formaldehyde mixing ratios and high water content of ambient air. Because of the use of relatively dry air in the chamber, and because of the high formaldehyde mixing ratios in the chamber (7–100 ppb), we were able to detect and calibrate for formaldehyde using the PTR-MS. Starting concentrations for acetaldehyde, acetone, and acetic acid were <5 ppb. Background counts were subtracted from the signal for all parent terpenes and oxidation products.

2.2. Cyclohexane Measurements

[14] Cyclohexane was used both as an OH scavenger and as the solvent for diluting pure terpene compounds for calibration. OH yields from the ozonolysis of biogenic terpenes have already been characterized [Aschmann *et al.*, 2002]. Cyclohexane was injected at sufficient concentrations so that the reaction of OH with cyclohexane exceeded that of OH with the terpene by a factor of 100. Cyclohexane was used because, as an alkane, it does not have a proton affinity high enough to be ionized and detected by PTR-MS, so the use of high concentrations of cyclohexane to scavenge OH would not saturate the instrument. However, the m/z 85 ion was detected and produced a linear response in the PTR-MS, but with a sensitivity to the cyclohexane concentration that was 1000 times lower than the sensitivity to monoterpenes. Thus, because of the high concentrations of cyclohexane used during the experiments, cyclohexane was likely detected at m/z 85. Additionally, reaction products from cyclohexane + OH reactions were detected by PTR-MS at significantly higher count rates compared to the terpene + O₃ oxidation products. The main oxidation products observed by PTR-MS from the reaction of cyclohexane + OH occurred at m/z 99 and 100, which indicated the formation of cyclohexanone and its ¹³C isotope (C₆H₁₀O). If any oxidation products from the terpene + O₃ reactions occurred on m/z 99 or 100, those signals would be smaller than and indistinguishable from the cyclohexanone. However, given the structures of the parent terpenes, C₁₀H₁₆, C₁₅H₂₄, C₁₀H₁₂O, C₁₀H₁₈O (see Figure 1), it seems unlikely that an unfragmented oxidation product from reactions with O₃ would occur significantly at m/z 99, which would require a formula of C₆H₁₀O or C₅H₆O₂. Cyclohexanone and cyclohexanol have been identified as the main products from cyclohexane + OH, with yields of 0.53 and 0.35 respectively [Berndt *et al.*, 2003]. Further reaction of cyclohexanol with OH results in additional formation of cyclohexanone with a yield of 0.58 [Berndt *et al.*, 2003]. Cyclohexanol was not detected by PTR-MS at its protonated parent mass (m/z 101), perhaps because the cyclohexanol becomes dehydrated at a 100% efficiency during the proton transfer reaction. The resulting dehydrated ion would occur at m/z 83, which is already swamped by interference from the cyclohexane impurities, thus the cyclohexanol was not quantifiable. The cyclohexoxy radical formed from cyclohexane + OH may also decompose by ring cleavage and isomerize to produce a hydroxy-dicarbonyl (C₆H₁₀O₃), with m/z of 131 that would dehydrate in the PTR-MS producing a fragment ion at m/z 113. Because m/z 113 was not observed ubiquitously as a product ion from all experiments, and m/z 131 was not observed as a product from any experiments, we conclude

that the C₆H₁₀O₃ hydroxy-dicarbonyl does not interfere with the signal observed at m/z 113. Additionally ozonolysis experiments without the use of cyclohexane were performed on α -pinene and β -pinene, and the yields of m/z 113 from α -pinene with and without cyclohexane were identical ($0.6 \pm 0.1\%$), and for β -pinene was $0.4 \pm 0.1\%$ with cyclohexane and $0.3 \pm 0.1\%$ without cyclohexane.

[15] The purity of the cyclohexane (Sigma-Aldrich, St. Louis, Missouri) used was 99.9%, with a 0.1% impurity that was detected by the PTR-MS predominantly at m/z 83 and 41 (Table 1). Although cyclohexene, occurring at m/z 83, is a likely candidate for the main cyclohexane impurity, the GC-FID did not detect any cyclohexene associated with the cyclohexane. This suggests that cyclohexene was not an impurity from cyclohexane and would not interfere with the terpene ozonolysis experiments. Another possible candidate for the cyclohexane impurity is cyclohexanol, as the ions associated with this compound are expected to be m/z 101 and 83. M/z 101 was not correlated with cyclohexane, thus, if the impurity is indeed cyclohexanol, it would require that the cyclohexanol become dehydrated at 100% efficiency in the PTR-MS. The signals of all additional masses associated with cyclohexane did not change during the terpene ozonolysis, indicating that these compounds were not interfering with the experiments by reacting with ozone and producing additional oxidation products. Masses listed in Table 1 in association with cyclohexane were not observed as fragments of the parent terpene compounds.

3. Results and Discussion

3.1. Aerosol Yields

[16] The initial experimental conditions and SOA yields are stated in Table 2. SOA mass yields from all compounds were calculated from the volumetric yields assuming an average aerosol density of 1.25 g cm⁻³ [Bahreini *et al.*, 2005; Ng *et al.*, 2006]. Yields of SOA varied significantly between the different terpene compounds. The terpene compounds listed in all tables are ordered with respect to decreasing aerosol yield. In general, the presence of an exocyclic double bond resulted in a reduction of SOA yield, compared to a compound with the same carbon number and an endocyclic double bond, supporting the results of Keywood *et al.* [2004b]. Terpene compounds with high aerosol yields (>40%) possessed one or more double bonds internal to the ring structure, such as 3-carene, α -terpinene, α -humulene, and α -pinene. β -caryophyllene, a sesquiterpene, has one internal and one external double bond, similar to terpinolene, but had higher SOA yields likely because of the lower volatility of the higher molecular weight oxidation products. Additionally, the oxidation of terpinolene at the external double bond results in the loss of 3 carbons, increasing the volatility of the terpinolene oxidation products, whereas the oxidation of β -caryophyllene at the external double bond results in the loss of one carbon. The ozonolysis of β -pinene, with one external double bond, resulted in intermediate SOA yields, and the reaction with ozone of the acyclic terpenes (myrcene and linalool) and methyl chavicol, with one external double bond and a benzene ring, resulted in the lowest aerosol yields.

[17] Table 2 compares SOA yields we obtained with those reported in the literature, and lists the OH scavengers and

Table 1. Molecular Weights Associated With Different Compounds Detected by PTR-MS

	<i>m/z</i> (mass + 1)	Structure	Description
Primary signal			
21		$\text{H}_2^{18}\text{OH}^+$	isotope of primary ion
37		$\text{H}_2\text{OH}_2\text{OH}^+$	primary ion water cluster
Cyclohexane ^a			
39, 40, 41, 43, 44, 53, 56, 57, 58, 69, 83, 84, 85, 86		$\text{C}_6\text{H}_{10}\text{OH}^+$	cyclohexane + OH oxidation product
Oxidation products from all ozonolysis experiments			
31		CH_2OH^+	formaldehyde
45		$\text{C}_2\text{H}_4\text{OH}^+$	acetaldehyde
47		$\text{CH}_2\text{O}_2\text{H}^+$	formic acid
59		$\text{C}_3\text{H}_6\text{OH}^+$	acetone
61		$\text{C}_2\text{H}_4\text{O}_2\text{H}^+$	acetic acid
3-carene			
81, 82, 137, 138 ^b		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
71, 73, 87, 89, 97, 107, 111 ^c , 113 [*] , 115, 123 [*] , 125, 127, 141 [*] , 151, 167, 169 ^d			unidentified oxidation products
α -terpinene			
81, 82, 137, 138		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
73, 87, 89, 107, 109, 113 [*] , 115, 123 [*] , 125, 127, 139, 141 [*] , 143, 151, 155 [*] , 157, 167, 171, 183, 185, 201			unidentified oxidation products
β -caryophyllene			
67, 68, 81, 82, 95, 109, 121, 137, 149, 205, 206		$\text{C}_{15}\text{H}_{24}\text{H}^+$	sesquiterpene, fragments, and isotopes
71, 73, 87, 115, 127, 133, 139, 151, 153, 159 [*] , 177, 197, 219, 223, 237, 253			unidentified oxidation products
α -humulene			
67, 81, 82, 95, 96, 97, 103, 109, 110, 121, 123, 135, 137, 149, 205, 206,		$\text{C}_{15}\text{H}_{24}\text{H}^+$	sesquiterpene, fragments, and isotopes
71, 73, 115, 125, 127, 129, 141 [*] , 197, 219, 221			unidentified oxidation products
α -pinene			
81, 82, 137, 138		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
71, 72, 107, 108, 123 [*] , 151, 152, 169, 170		$\text{C}_{10}\text{H}_{16}\text{O}_2\text{H}^+$	uncalibrated oxidation product: pinonaldehyde, fragments, and isotopes ^e
73, 75, 79, 87, 97, 111 [*] , 113 [*] , 115, 117, 125, 127, 129, 133, 139, 141 [*] , 143, 147, 155 [*] , 165, 167, 171, 183, 185			unidentified oxidation products
Terpinolene			
81, 82, 137, 138		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
71, 73, 87, 93, 109, 111 [*] , 113 [*] , 115, 125, 127, 129, 141 [*] , 143, 157, 167			unidentified oxidation products
β -pinene			
81, 82, 137, 138		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
97, 103, 121, 122, 139, 140, 141 [*]		$\text{C}_9\text{H}_{14}\text{OH}^+$, $\text{C}_9\text{H}_{12}\text{H}^+$	calibrated oxidation product: nopinone, isotopes and fragments
107, 109, 111 [*] , 113, 119, 123 [*] , 125, 129, 153, 155 [*] , 169 [*] , 171, 185			unidentified oxidation products
Myrcene			
81, 82, 137, 138		$\text{C}_{10}\text{H}_{16}\text{H}^+$, $\text{C}_6\text{H}_9\text{H}^+$	monoterpene, fragments and isotopes
71, 73, 75, 79, 93, 97, 111 [*] , 113 [*] , 115, 127, 139			unidentified oxidation products
Methyl chavicol			
149, 150		$\text{C}_{10}\text{H}_{12}\text{OH}^+$	oxygenated terpene and isotope
109, 115, 121, 125, 137, 151 [*] , 152, 163			unidentified oxidation products
Linalool			
81, 82, 137, 138, 155, 156		$\text{C}_{10}\text{H}_{18}\text{OH}^+$, $\text{C}_{10}\text{H}_{16}\text{H}^+$	oxygenated terpene, fragments, and isotopes
73, 75, 93, 94, 111 [*] , 113 [*] , 115, 127, 128, 129, 130			unidentified oxidation products

^aMasses associated with cyclohexane listed in bold font were >10% of the parent ion *m/z* 85.^bAll monoterpenes occur predominantly on the parent *m/z* 137 and the fragment *m/z* 81 ions, with a small fraction (<20%) occurring on the ¹³C isotope with *m/z* (138, 82).^cAsterisks following unidentified oxidation products represent unidentified ions that were observed in the canopy air of a coniferous forest in California by PTR-MS [Holzinger et al., 2005].^dUnidentified oxidation products in bold font represent ions with >5% yield (on a mole basis) from the parent terpene.^eFragments were determined from correlations with *m/z* 151 (the dominant pinonaldehyde ion), and agreed well with fragmentation patterns reported elsewhere for pinonaldehyde [Wishtaler et al., 2001].

Table 2. Initial Conditions and SOA Yields Obtained From This Study Compared With Results From Other Dark Ozonolysis Experiments

Temperature, K	RH, %	ΔHC , ppb	$\Delta\text{M}_{\text{O}_3}$, $\mu\text{g m}^{-3}$	OH Scavenger	SOA Mass Yield, % ^a	Reference
3-carene						
293	6.5	90 $\pm$ 3	271 $\pm$ 4	cyclohexane	54 $\pm$ 2	this work
306			63	2-butanol	13	[Yu <i>et al.</i> , 1999a]
306–310			6–64	2-butanol	8–13	[Griffin <i>et al.</i> , 1999]
290			390	none	76	[Hoffmann <i>et al.</i> , 1997]
α -terpinene						
293	3.4	61 $\pm$ 1	164 $\pm$ 1	cyclohexane	47 $\pm$ 1	this work
β -caryophyllene						
293	6.2	88 $\pm$ 4	336 $\pm$ 3	cyclohexane	45 $\pm$ 2	this work
287–290	80–85			none	39	[Jaoui <i>et al.</i> , 2003] ^b
α -humulene						
293	4.5	111 $\pm$ 6	415 $\pm$ 3	cyclohexane	45 $\pm$ 3	this work
α -pinene						
292	4.1	186 $\pm$ 8	417 $\pm$ 5	cyclohexane	41 $\pm$ 2	this work
306–308			40–65	2-butanol	16–19	[Yu <i>et al.</i> , 1999a]
306–308				none	16	[Winterhalter <i>et al.</i> , 2003]
303–310			8–65	2-butanol	8–19	[Griffin <i>et al.</i> , 1999]
319–322			38–154	none	14–23	[Hoffmann <i>et al.</i> , 1997]
289			341	none	67	[Hoffmann <i>et al.</i> , 1997]
terpinolene						
293	5.5	112 $\pm$ 3	124 $\pm$ 2	cyclohexane	20 $\pm$ 1	this work
β -pinene						
293	6.3	180 $\pm$ 4	174 $\pm$ 3	cyclohexane	17 $\pm$ 1	this work
306–307			11–19	2-butanol	4–8	[Yu <i>et al.</i> , 1999a]
306–308			12–80	2-butanol	0–5	[Griffin <i>et al.</i> , 1999]
292			97	none	32	[Hoffmann <i>et al.</i> , 1997]
293–295				none	26	[Jaoui and Kamens, 2003] ^c
myrcene						
293	6.7	98 $\pm$ 3	61 $\pm$ 2	cyclohexane	11 $\pm$ 1	this work
methyl chavicol						
292	4.5	101 $\pm$ 3	40 $\pm$ 2	cyclohexane	6 $\pm$ 0.4	this work
linalool						
292	4.0	106 $\pm$ 5	8 $\pm$ 2	cyclohexane	1 $\pm$ 0.2	this work
290			39.5	none	8	[Hoffmann <i>et al.</i> , 1997]

^aSOA yields are expressed on a percent mass basis, using the ratio of μg organic aerosol m^{-3} to μg terpene m^{-3} , and assuming an aerosol density of 1.25 g cm^{-3} .

^bPercent molar yield from 16 July 2000 experiment, with air temperatures most similar to the work reported here.

^cThese experiments were performed in the daylight in the presence of NO_x .

conditions used for the different experiments. The effect of temperature on SOA production is well known, with higher SOA yields resulting from experiments conducted at lower temperature, however, the compounding effects of temperature, RH, hydrocarbon consumption, and scavenger use make it difficult to compare SOA yield with other experiments. Recently, UV radiation was found to reduce SOA yield from α -pinene ozonolysis by a constant absolute reduction of ~ 0.03 , or 3% [Presto *et al.*, 2005a], which does not affect comparisons with other dark ozonolysis experiments, but is expected to reduce the SOA yield of α -pinene, and perhaps other terpenes, in the ambient atmosphere. Additionally, high NO_x levels in α -pinene ozonolysis experiments were shown to dramatically reduce SOA yields as the $\text{VOC}:\text{NO}_x$ ratio decreased [Presto *et al.*, 2005b], however, its significance to the real atmosphere is site-dependent and may not be applicable to forested or remote regions with low NO_x concentrations.

[18] Jaoui *et al.* [2003] reported a lower SOA yield of 39% from the ozonolysis of β -caryophyllene, without the use of an OH scavenger under slightly lower air temperatures and higher RH (80–85%) than used here. These conditions are both expected to increase SOA yield compared to the yield we observed, however, those experiments

were conducted so that O_3 concentrations were depleted and approached 0 ppm, which may not have allowed for the further oxidation of the reported gas-phase oxidation products that still contained a double bond, suggesting the important contribution of second generation products in SOA yield. Thus perhaps the incomplete ozonolysis of all the gas-phase oxidation products resulted in the lower SOA yield observed by Jaoui *et al.* [2003].

[19] It is notable that the photo-oxidation of sesquiterpenes has been reported to result in a very high SOA yield, even when the photo-oxidation occurred at very high air temperatures. The photo-oxidation of β -caryophyllene resulted in $>100\%$ SOA yields at temperatures ranging from 316–322 K [Hoffmann *et al.*, 1997], and SOA yields from β -caryophyllene and α -humulene were ~ 30 –80% under temperatures ranging from 306–310 K [Griffin *et al.*, 1999]. The shorter lifetime of sesquiterpenes with respect to ozone (~ 1 min at 50 ppb O_3) than OH (30–40 min at 2×10^6 molecules cm^{-3} OH) suggests that sesquiterpene ozonolysis experiments may be more relevant to the atmosphere since ozone oxidation is likely to be the dominant loss process. The SOA yields from sesquiterpenes presented here, and reported by Jaoui *et al.* [2003], suggest that the ozonolysis of β -caryophyllene results in high ($\sim 45\%$), but not extraordinarily high ($\sim 100\%$), yield

Table 3. Gas-Phase Molar Yields and Carbon Balance (%) for the Ozonolysis Experiments

Terpene	Formaldehyde,% Yield	Acetaldehyde,% Yield	Formic Acid,% Yield	Acetone,% Yield	Acetic Acid, % Yield	UnID, ^a % Yield	C Balance, ^b %
3-carene	25 ± 2	3.9 ± 0.4	11 ± 1	9.5 ± 1	14 ± 1	19 ± 1	55 ± 2
α-terpinene	4 ± 2	1 ± 0.3	9.6 ± 2	6.3 ± 1	9.5 ± 2	31 ± 2	58 ± 4
β-caryophyllene ^c	76 ± 20	0.9 ± 0.3	3.9 ± 1	1.1 ± 0.3	20 ± 5	6.4 ± 0.8	39 ± 2
α-humulene ^c	3.5 ± 1.1	0.9 ± 0.3	0.4 ± 0.2	1.2 ± 0.4	12 ± 1	9.5 ± 0.8	33 ± 2
α-pinene ^d	28 ± 3	2.9 ± 0.3	7.5 ± 0.7	5.9 ± 0.5	8 ± 0.9	15 ± 1	67 ± 3
terpinolene	29 ± 3	9 ± 0.8	4 ± 0.4	44 ± 4	5.8 ± 0.6	81 ± 9	77 ± 13
β-pinene ^d	65 ± 6	2.4 ± 0.2	4 ± 0.4	3.6 ± 0.3	8.6 ± 0.9	20 ± 1	54 ± 3
myrcene	51 ± 5	15 ± 2	3.9 ± 0.4	23 ± 2	5.3 ± 0.5	92 ± 10	69 ± 14
methyl chavicol	61 ± 5	...	11 ± 1	1.1 ± 0.1	2.2 ± 0.3	50 ± 7	55 ± 8
linalool	34 ± 3	14 ± 1	2.5 ± 0.3	16 ± 1	5.1 ± 0.5	92 ± 9	63 ± 13

^aSum of the yields of all product ions (m/z) listed in Table 1.

^bThe carbon balance (%) from identified gas-phase products (formaldehyde, formic acid, acetaldehyde, acetone, nopinone, and pinonaldehyde), plus the yield of the unidentified compounds, assuming a conservative number of C for each observed ion, and from the particle-phase, assuming the SOA is 60% C. The pinonaldehyde yield used for the C balance calculation was the lower-limit yield of 19%.

^cSeed aerosol was not used in the sesquiterpene experiments.

^dFrom α-pinene ozonolysis, the percent molar yield of pinonaldehyde was estimated to range from 19 ± 2% to 34 ± 3% (see text) and the molar yield of α-pinene oxide was 5.4 ± 0.6%. From β-pinene ozonolysis the yield of nopinone from was 17 ± 2%.

of SOA, and may not be considerably higher than the SOA yield from monoterpenes.

3.2. Gas-Phase Yields of Low Molecular Weight Products

[20] Molar yields of gas-phase products are shown in Table 3, and a comparison with yields obtained in other studies is shown in Table 4. Yields were calculated as the slope of the least squares regression between the change in concentration of oxidation product and the change in concentration of the parent hydrocarbon. The uncertainty estimates presented in Table 3 are the standard errors of the estimated slope of the regression that also include the systematic uncertainties described in the Experimental section. For the oxidation products that peaked and decreased with time resulting from further oxidation or partitioning into the particle phase, the linear least squares regressions excluded data points after the peak in concentration. From this work, the highest yields of formaldehyde were observed from the ozonolysis of β-caryophyllene, β-pinene, myrcene, and methyl chavicol. β-caryophyllene, β-pinene, and methyl chavicol each have an external double bond, while myrcene is acyclic, with three double bonds. Conversely, very low formaldehyde yields were observed from α-humulene (3.5 ± 1%) and α-terpinene (4 ± 2%), both with multiple internal double bonds. Yields of acetaldehyde, formic acid, and acetic acid were <20% for all terpene compounds. Formic acid yields from terpene oxidation by OH were reported at <10% [Orlando *et al.*, 2000], however, we are not aware of other studies reporting yields of formic acid, acetic acid, or acetaldehyde from terpene ozonolysis. Acetone yields ranged from 1% from methyl chavicol and β-caryophyllene to 44% from terpinolene. Acetone yields have been reported from several different terpene compounds [Reissell *et al.*, 1999; Orlando *et al.*, 2000], and from β-pinene [Jaoui and Kamens, 2003] and linalool [Shu *et al.*, 1997], and are in reasonable agreement with yields obtained here (Table 4).

[21] Different analytical methods were used to determine the concentrations and yields of the low molecular weight oxidation products from different studies. The concentrations reported here were obtained using calibrations performed on the PTR-MS, however, because compounds are

detected by the PTR-MS according to their mass to charge ratio (m/z), compounds with the same molecular weight are indistinguishable. The calibrations of the parent terpenes and the identified oxidation products (except pinonaldehyde), which used SilcoSteel tubing of a similar length as the tubing used for chamber sampling, corrected for potential losses of sticky compounds, such as the sesquiterpenes, or low molecular weight acids, in the tubing. Thus underestimation of calibrated compounds due to loss in the tubing should be minimal, and concentrations and yields of calibrated compounds reported here should be considered an upper limit, as we operate on the assumption that the entire signal comes from the expected compound without interference. This assumption is likely valid for the parent terpenes and the low molecular weight oxidation products, as relatively few compounds, that might be expected from these oxidation experiments, share the same m/z as formaldehyde (m/z 31), acetaldehyde (m/z 45), formic acid (m/z 47), acetone (m/z 59), and acetic acid (m/z 61). For the larger oxidation products, reported according to their m/z , we cannot determine if one particular compound completely represents an observed oxidation product mass, because different oxidation products can share the same molecular weight, as seen with m/z 153 and 155 from β-pinene ozonolysis (Table 4). Thus the yields observed in this study of unidentified oxidation products, reported according to their m/z , are lower limits of the actual yields of a given m/z . Additionally, the inability to calibrate the higher molecular weight oxidation products against known standards means fragmentation patterns are not fully known, and implies that sticky oxidation products, such as the higher molecular weights acids, might be lost in the tubing and thus underestimated, affecting our ability to close the carbon mass balance of the system (Table 3). Interference by cyclohexane and its oxidation products on several m/z also inhibits our ability to detect terpene oxidation products occurring at those m/z .

[22] Generally, higher partitioning of oxidation products into the particle phase should be balanced by lower partitioning of oxidation products in the gas phase. Table 3 lists the molar yields of unidentified oxidation products and shows the expected general trend of higher molar yields of unidentified gas-phase products from terpenes with lower

Table 4. Comparison of Gas Phase Oxidation Product Yields, on a Percent Mole Basis, Observed in This Study With Results From Other Terpene Ozonolysis Experiments Conducted in the Dark

Product	Product Yield, %, This Work	Product Yield, %, Other Studies	Reference
3-carene			
Acetone	9.5	10	[Orlando et al., 2000]
Acetone	9.5	22–23	[Reissell et al., 1999]
<i>m/z</i> 169	0.3	trace ^a	[Hakola et al., 1994]
α -terpinene			
Acetone	4.4	2–3	[Reissell et al., 1999]
β -caryophyllene			
Formaldehyde	76	80	[Grosjean et al., 1993]
α -pinene			
Acetone	5.9	3	[Orlando et al., 2000]
Acetone	5.9	6–8	[Reissell et al., 1999]
Pinonaldehyde	19–34 ^b	6–18	[Yu et al., 1999a]
Pinonaldehyde	19–34 ^b	14	[Alvarado et al., 1998]
Pinonaldehyde	19–34 ^b	16	[Baker et al., 2001]
Pinonaldehyde	19–34 ^b	19	[Hakola et al., 1994]
Pinonaldehyde	19–34 ^b	23 (dry)	[Warscheid and Hoffmann, 2001]
Pinonaldehyde	19–34 ^b	32 (higher RH)	[Berndt et al., 2003]
Pinonaldehyde	19–34 ^b	42 (lower RH)	[Berndt et al., 2003]
Pinonaldehyde	19–34 ^b	53 (RH ~ 60%)	[Warscheid and Hoffmann, 2001]
<i>m/z</i> 153	5.4 $\pm$ 0.6 ^c	2.1 ^d	[Alvarado et al., 1998]
<i>m/z</i> 153	5.4 $\pm$ 0.6 ^c	3 ^d	[Berndt et al., 2003]
<i>m/z</i> 155	0.3 $\pm$ 0.1	1.1–2.4 ^e	[Yu et al., 1999a]
<i>m/z</i> 171	0.1 $\pm$ 0.02	2.2–9.8 ^f	[Yu et al., 1999a]
<i>m/z</i> 185	0.05 $\pm$ 0.02	0.6–6.6 ^g	[Yu et al., 1999a]
Terpinolene			
Acetone	44	50	[Orlando et al., 2000]
Acetone	44	48–50	[Reissell et al., 1999]
<i>m/z</i> 111, 93	53 $\pm$ 9 ^h	40	[Hakola et al., 1994]
β -pinene			
Formaldehyde	65	42	[Grosjean et al., 1993]
Formaldehyde	65	65 (higher RH)	[Winterhalter et al., 1999]
Formaldehyde	65	77	[Jaoui and Kamens, 2003]
Formaldehyde	65	84 (dry)	[Winterhalter et al., 1999]
Acetone	3.6	0.9	[Orlando et al., 2000]
Acetone	3.6	2–7	[Reissell et al., 1999]
Acetone	3.6	5	[Jaoui and Kamens, 2003]
Nopinone	17	16 (dry)	[Winterhalter et al., 1999]
Nopinone	17	16–17	[Yu et al., 1999a]
Nopinone	17	21	[Jaoui and Kamens, 2003]
Nopinone	17	22	[Grosjean et al., 1993]
Nopinone	17	23 (5% RH)	[Hakola et al., 1994]
Nopinone	17	35 (higher RH)	[Winterhalter et al., 1999]
Nopinone	17	40	[Hatakeyama et al., 1989]
<i>m/z</i> 153	6.1 $\pm$ 1	1.9–4.5 ⁱ	[Jaoui and Kamens, 2003]
<i>m/z</i> 153	6.1 $\pm$ 1	2–8 ^j	[Yu et al., 1999a]
<i>m/z</i> 155	4.7 $\pm$ 1	5.3–8.1 ^k	[Jaoui and Kamens, 2003]
<i>m/z</i> 155	4.7 $\pm$ 1	7–8 ^l	[Yu et al., 1999a]
<i>m/z</i> 171	0.1 $\pm$ 0.03	4.6–14.3 ^f	[Yu et al., 1999a]
<i>m/z</i> 185	1.1 $\pm$ 0.3	0.4–0.6 ^g	[Yu et al., 1999a]
Myrcene			
Formaldehyde	51	26	[Ruppert et al., 1997]
Acetone	23	21	[Reissell et al., 2002]
Acetone	23	25	[Orlando et al., 2000]
Acetone	23	29	[Ruppert et al., 1997]
<i>m/z</i> 75	16 $\pm$ 4 ^m	33–38	[Reissell et al., 1999]
<i>m/z</i> 75	16 $\pm$ 4 ^m	19	[Ruppert et al., 1997]
<i>m/z</i> 111 + 93	49 $\pm$ 8 ⁿ	70	[Reissell et al., 2002]
Linalool			
Formaldehyde	34	36	[Shu et al., 1997]
Acetone	16	21	[Shu et al., 1997]
<i>m/z</i> 127	11 $\pm$ 2	12.6 ^o	[Shu et al., 1997]
<i>m/z</i> 129, 111, 93	50 $\pm$ 9 ^p	85 ^q	[Shu et al., 1997]

^aYield of caronaldehyde.^bEstimated yield (see text).^cUpper limit yield of α -pinene oxide based on the calibrated concentration calculated from *m/z* 153.^dYield of α -pinene oxide.^eYield of norpinonaldehyde.^fYield of norpinonic acid.^gYield of pinonic acid.^hYield of 4-methyl-3-cyclohexenone (C₇H₁₀O = 110 amu).ⁱSum of molar yields of reported products with molecular weight of 152, i.e., 3-oxonopinone, β -pinene oxide, and myrtenol.

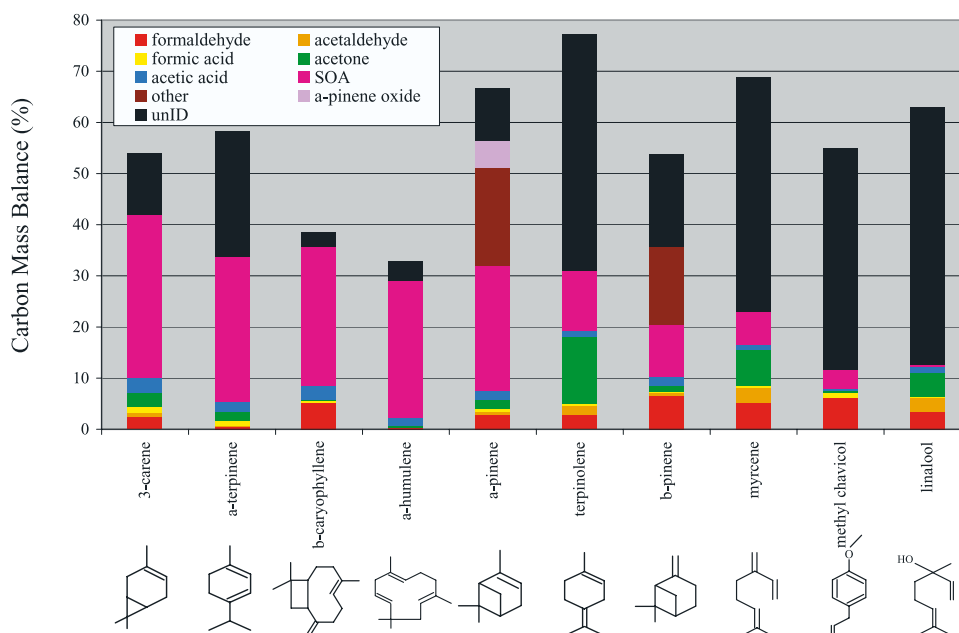


Figure 2. Carbon mass balance for each experiment. SOA was assumed to be 60% C, and carbon numbers were assumed for each unidentified product ion listed in Table 1. For α -pinene, “other” refers to the lower-limit yield of pinonaldehyde, and for β -pinene, “other” refers to nopinone.

SOA yields. The notable exceptions are α - and β -pinene, with low unidentified molar yields because of the identification of pinonaldehyde, α -pinene oxide, and nopinone, the dominant oxidation products, and β -caryophyllene and α -humulene, with very low unidentified m/z yields (<10%) because of fragmentation and loss of the higher molecular weight oxidation products. The carbon balance for each experiment (Table 3 and Figure 2) was calculated by summing the SOA yield, assuming the aerosol is 60% carbon, the yields of the calibrated oxidation products: formaldehyde, acetaldehyde, formic acid, acetone, acetic acid, nopinone and α -pinene oxide, and the estimated oxidation product: pinonaldehyde, and the yields of unidentified compounds, assuming the number of carbons for each oxidation product ion (Table 1). Without including the unidentified ions, we only accounted for 12–56% of the carbon from the reacted terpenes. With the unidentified compound ions included, the carbon balance only increased to 33–77%.

3.3. Gas-Phase Yields of High Molecular Weight Products

[23] We observed a nopinone yield of 17% from β -pinene ozonolysis, which agrees well with yields from other studies, which typically range from 16–22% (Table 4).

The initial reaction between ozone and β -pinene is known to form a primary ozonide (POZ) that decomposes into either a C_1 -Criegee intermediate (CI) + nopinone, or a C_9 -CI + formaldehyde [e.g., Winterhalter *et al.*, 1999, and references therein]. Thus nopinone and formaldehyde represent the only two possible channels for the decomposition of the POZ, and should sum to unity [Winterhalter *et al.*, 1999]. We observed a sum of the two carbonyls of $82 \pm 6\%$, suggesting that we may be underestimating yields of the sum of these two compounds by $\sim 20\%$.

[24] Pinonaldehyde yields from α -pinene ozonolysis were estimated by summing the calculated concentrations of pinonaldehyde-associated ions (Table 1) according to equation (1). The pinonaldehyde fragment ions were determined by finding the m/z that exhibited strong correlations ($R^2 > 0.8$) with m/z 151, the dominant pinonaldehyde ion. These fragment ions are listed in Table 1 and agree well with those described elsewhere [Wisthaler *et al.*, 2001]. Several of the ions reported by Wisthaler *et al.* [2001], m/z 43, 81, and 99 were not well correlated with m/z 151 because of interference from other compounds. Additionally, several ions listed in Table 1, m/z 71, 72, and 109, exhibited highly elevated slopes in the regression against 151 compared to those reported by Wisthaler *et al.* [2001]. Because the pressure of the reaction chamber in the PTR-MS determines

Notes to Table 4.

^jMolar yield of 3-oxonopinone.

^kSum of molar yields of reported products with molecular weight of 154, i.e., 1-hydroxynopinone (4.1%) and 3-hydroxynopinone (3.5%).

^lYield of the hydroxynopinones.

^mYield of hydroxyacetone ($C_3H_6O_2 = 74$ amu).

ⁿYield of 4-vinyl-4-pentenal ($C_7H_{10}O = 110$ amu).

^oYield of 5-ethenyldihydro-5-methyl-2(3H)-furanone ($C_7H_{10}O_2 = 126$ amu).

^pThe sum of m/z 129, 111, and 93 were used in the comparison with the 4-hydroxy-4-methyl-5-hexen-1-al yield and 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran because of the likely dehydration of the hydroxyl and aldehyde groups from the parent (m/z 129) ion in the PTR-MS.

^qYield of 4-hydroxy-4-methyl-5-hexen-1-al ($C_7H_{12}O_2 = 128$ amu).

Table 5. Percent Yield, on a Mole Basis, of Oxidation Product Ions From Terpene Ozonolysis That Were Also Observed in Ambient Air Within a Ponderosa Pine Canopy in California

Terpene	<i>m/z</i> 111	<i>m/z</i> 113	<i>m/z</i> 123	<i>m/z</i> 141	<i>m/z</i> 151	<i>m/z</i> 155	<i>m/z</i> 159	<i>m/z</i> 169
3-carene	1.5 ± 0.3	1 ± 0.2	1.5 ± 0.3	2.4 ± 0.5	0.5 ± 0.1			
α-terpinene		1.3 ± 0.3	2.5 ± 0.6	1.4 ± 0.3	1 ± 0.3	1.2 ± 0.3		1.3 ± 0.3
<i>β-caryophyllene</i> ^a							0.3 ± 0.1	
<i>α-humulene</i> ^a				0.3 ± 0.1				
α-pinene	0.4 ± 0.1	0.6 ± 0.1		0.7 ± 0.2		0.3 ± 0.1		
Terpinolene	53 ± 9^b	2.8 ± 0.6		0.6 ± 0.1				
β-pinene	1.1 ± 0.3	0.4 ± 0.1	0.5 ± 0.3			4.7 ± 1		0.5 ± 0.1
Myrcene	50 ± 8^b	5.2 ± 1.2						
Methyl chavicol					25 ± 6			
<i>Linalool</i> ^a	50 ± 9^c	1.5 ± 0.3						

^aThe terpenes listed in italics have not been measured in the air above the Blodgett Forest canopy. The short lifetime of the two sesquiterpenes, *β-caryophyllene* and *α-humulene* likely affect their detection in ambient air above the canopy, and linalool, typically associated with flowering citrus plants, may not be emitted at all from Blodgett Forest.

^bThe yield of *m/z* 111 represents the sum of the yields from *m/z* 111 and *m/z* 93. Yields listed in bold are yields greater than 10%, and all yields of unidentified product ions represent a lower limit because of lack of knowledge about fragmentation.

^cThe yield of *m/z* 111 represents the sum of the yields of *m/z* 129, 111, and 93.

the degree of fragmentation of the parent compound, we do not expect our fragmentation patterns to be identical to those reported by *Wisthaler et al.* [2001]. We operated the reaction chamber of the PTR-MS at a 2.1 mbar, higher than the 2.0 mbar used by *Wisthaler et al.* [2001]. Thus we expected increased fragmentation of pinonaldehyde, and we accordingly observed a lower proportion of *m/z* 169 to 151, and higher proportions of all other fragments listed in Table 1 to *m/z* 151. The lower-limit pinonaldehyde yield of 19 ± 2% was calculated by summing the concentrations of the ions, *m/z* 107, 108, 123, 151, 152, 169, and 170, that were within 2 times the fractions reported in *Wisthaler et al.* [2001]. The upper limit pinonaldehyde yield of 32 ± 3% includes *m/z* 71, 72, and 109, with proportions relative to *m/z* 151 that were more than three times larger than those reported by *Wisthaler et al.* [2001]. Including the contribution to the total pinonaldehyde signal from *m/z* 43, 81, and 99, using the proportions relative to *m/z* 151 [*Wisthaler et al.*, 2001], would increase the pinonaldehyde yield by ~2%. Our pinonaldehyde yield is quite uncertain, but should be in the range of 19–34%. Both the lower and upper limit yields are within the range of yields reported elsewhere (Table 4).

[25] Yields of pinonaldehyde from α-pinene + O₃ reactions were reported to be higher under high RH by *Warscheid and Hoffmann* [2001], and higher under drier conditions by *Berndt et al.* [2003]. However, pinonaldehyde yields were also found to be relatively independent of water over an RH range of 5–50%, and independent of the OH scavenger (cyclohexane versus 2-butanol) used [*Baker et al.*, 2001]. The experiments reported here were conducted under low RH (4% for α-pinene), relatively low temperatures (293 K), and intermediate starting concentrations of parent terpenes compared to other studies. While our initial conditions are most similar to those of *Yu et al.* [1999a], our estimated pinonaldehyde yield of 19–34% is more similar to the yields obtained under the dry conditions by *Warscheid and Hoffmann* [2001]. The lower-range pinonaldehyde yields reported by *Yu et al.* may be a result of the use of a denuder and derivatization techniques for gas-phase measurements, compared to the direct sampling and analysis using PTR-MS (this study), FT-IR [*Berndt et al.*, 2003], and APCI-MS [*Warscheid and Hoffmann*, 2001].

[26] Yields of the unidentified oxidation products reported according to their *m/z* can be tentatively compared with gas-

phase yields of carbonyls and carboxylic acids reported elsewhere (Table 4). The yields of ions associated with carbonyl compounds generally agree well those from other studies, but our yields of ions from carboxylic acids are lower than those reported elsewhere, likely because tubing losses. A few studies have observed carbonyl, hydroxyl-carbonyl, and acidic monoterpene oxidation products in the gas and particle phase collected from ambient air of a forested environment [*Yu et al.*, 1999b; *Kavouras et al.*, 1999]. Recently *Holzinger et al.* [2005] reported on measurements of oxidation products in the forest canopy using PTR-MS. They identified several ions exhibiting diurnal cycles and vertical profiles in the canopy that are suggestive of oxidation products that partition into the particle phase (nopinone and pinonaldehyde, and *m/z* 105, 123, 155, and 159), or that are formed from rapid oxidation of primary terpene compounds within the forest canopy at Blodgett Forest (e.g., *m/z* 111, 113, 123, and 141) [*Holzinger et al.*, 2005]. Many of these ions were also observed from these terpene ozonolysis experiments, and are followed by an asterisk in Table 1. Of these unidentified compounds in the forest canopy, *m/z* 113 was dominant, with typical mixing ratios of 0.5 ppb at a height of 6–8 m, which was directly above the canopy. The mixing ratios of *m/z* 111 were highest within the forest canopy, typically reaching 0.14 ppb. Table 5 shows that percent yields, on a mole basis, were highest of *m/z* 111 + *m/z* 93 from terpinolene and myrcene, 53 ± 9% and 50 ± 8%, respectively. Yields of *m/z* 113 were much lower, ranging from 1 to 5% from the six different terpenes (Table 5). Although the higher yields of *m/z* 111 than *m/z* 113 from myrcene and terpinolene seems to contradict the higher mixing ratios of *m/z* 113 than 111 observed at Blodgett Forest, the time evolution of these two compounds (Figures 3 and 4) shows that *m/z* 111 was not a stable product, but underwent further oxidation, whereas *m/z* 113 was stable over the course of the experiment, suggesting that *m/z* 111 produced in the canopy would quickly undergo further oxidation, leading to lower mixing ratios in the canopy than expected on the basis of the maximum gas-phase yield. Of the three terpenes with high yields of *m/z* 113, terpinolene, myrcene, and α-terpinene have been reported from Blodgett Forest, but represent a small fraction of the monoterpene emissions measured above the canopy [*Lee et al.*, 2005]. However, above-canopy

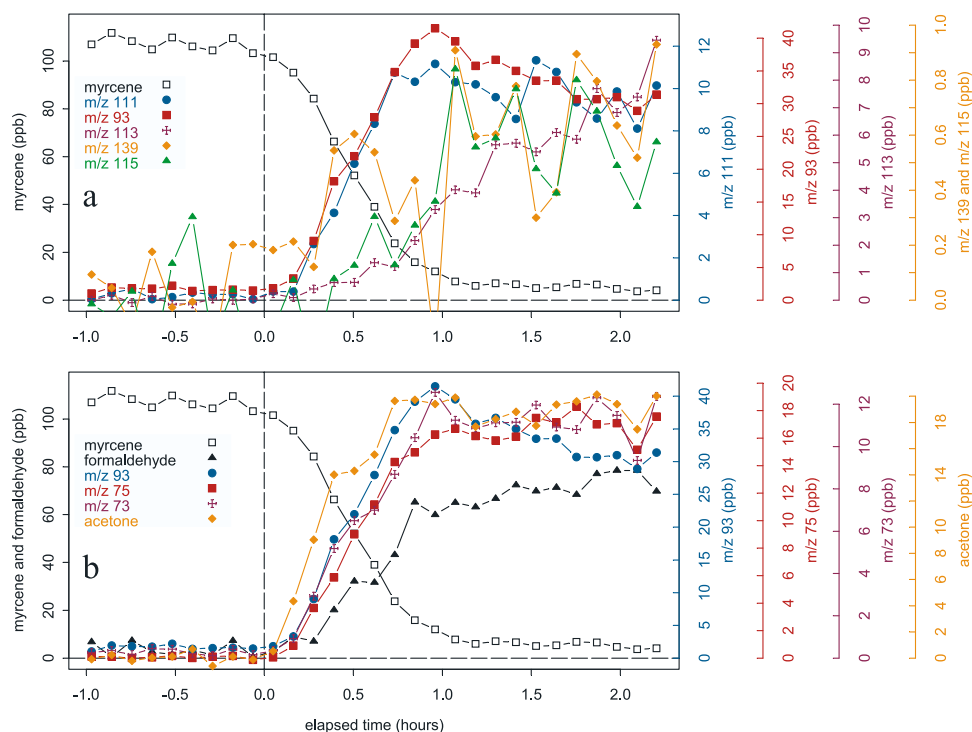


Figure 3. (a) Time series of myrcene ozonolysis and oxidation products for which structures are proposed (Figure 6). (b) Additional product ions, m/z 75 and 73, are also formed quickly, but unlike m/z 93, did not decrease over the course of the experiment.

measurements of concentration and flux only detect the terpene compounds that escape the forest canopy without undergoing within-canopy oxidation. Thus product ions detected inside the forest canopy likely come from the

oxidation of terpene compounds that do not escape the forest canopy, or perhaps escape in small quantities and are detected above the canopy at low mixing ratios. Comparisons between the gas-phase yields of unidentified

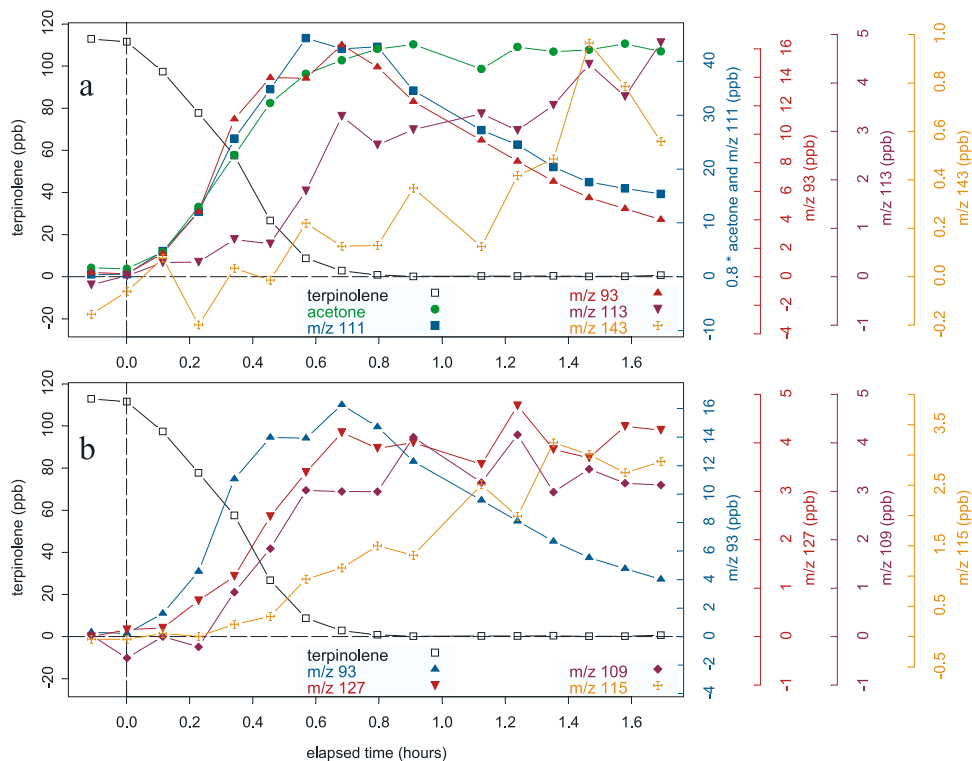


Figure 4. (a) Time series of terpinolene ozonolysis and oxidation product ions for which structures are proposed (Figure 7). (b) Additional product ions, m/z 127, 109, and 115, are formed later than m/z 93.

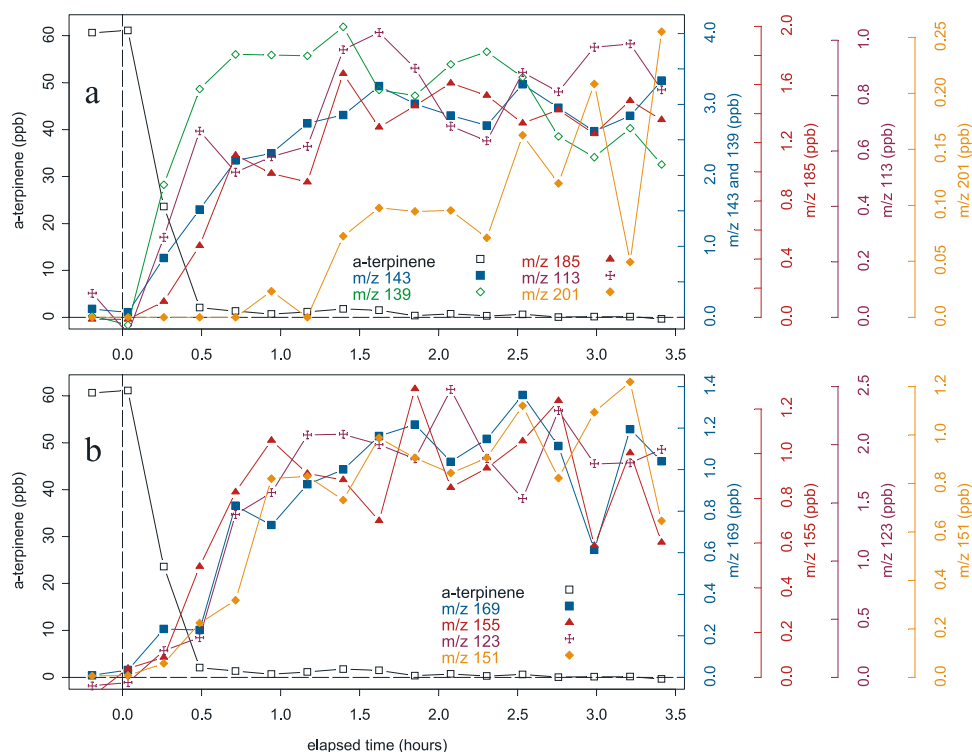


Figure 5. (a) Time series of α -terpinene ozonolysis and oxidation product ions for which structures are proposed (Figure 8). (b) Additional product ions were observed at low concentrations that continued to increase after complete consumption of α -terpinene.

oxidation products observed from these experiments and concentrations of product ions in the forest canopy cannot be quantitative without knowledge of the actual emission rates of all terpene compounds in the absence of oxidative chemistry. However, the information in Table 1 of the product ions detected from these ozonolysis experiments, can be qualitatively compared with ions observed in the forest canopy to suggest that those compounds observed in the forest canopy are likely oxidation products from terpene oxidation, and the information in Table 5 can quantitatively confirm that the 10–50% yield estimate used by Holzinger *et al.* [2005] to calculate the original emission rate of precursor terpenes was reasonable. However, a better constrained estimate of the emission rate requires knowledge of the actual mix of very reactive terpene compounds emitted from the forest, since yields of identified and unidentified oxidation products vary significantly between different terpene species (Tables 3 and 5).

[27] Because many oxidation mechanisms and products have been described in detail elsewhere [e.g., Winterhalter *et al.*, 1999; Baker *et al.*, 2001; Jaoui *et al.*, 2003; Docherty *et al.*, 2005], we will focus the time series data on myrcene, terpinolene, and α -terpinene. These monoterpenes are more reactive with O_3 than OH ($\tau_{\text{myrcene}} \sim 28$ min, $\tau_{\text{terpinolene}} \sim 7$ min, and $\tau_{\alpha\text{-terpinene}} \sim 0.6$ min with respect to 50 ppb O_3), were observed in a forested atmosphere [Lee *et al.*, 2005], produced oxidation products with mass to charge ratios that were observed at the same site by Holzinger *et al.* [2005], and represent the spectrum of low, middle, and high yields of SOA. The partial oxidation mechanisms shown for these three compounds are not

intended to be an exhaustive presentation of all oxidation product ions reported in Table 1, nor do they include all possibilities for Criegee intermediates, but rather focus on the dominant oxidation product ions, and the ions that were observed by Holzinger *et al.* [2005].

3.4. Time Evolution of Gas-Phase Products

[28] Figures 3–5 show the time series graphs of myrcene, terpinolene, and α -terpinene, and represent 8–15 min averages of data collected by PTR-MS, depending on the scan time of the particular experiment. Figures 3a, 4a, and 5a show the loss of the parent terpene compound and the rise in concentration of oxidation products for which reasonable structures and mechanisms are suggested in Figure 6–8. Figures 3b, 4b, and 5b show the production of other interesting oxidation product ions for which structures or formation mechanisms could not readily be determined.

3.4.1. Myrcene

[29] The time series of myrcene ozonolysis (Figure 3a) shows multistep oxidation processes in real time: many products are formed quickly (acetone, m/z 111, 93, and 139) and other products are formed more slowly (formaldehyde, m/z 113 and 115). The similar change with time in the concentration of m/z 111 and 93 (linear least squares regression $R^2 = 0.99$), and their 18 amu mass difference, suggest that m/z 93 is a dehydrated fragment of m/z 111. Proposed structures for these product ions are shown in Figure 6. The production of 4-vinyl-4-pentenal (MW = 110 amu) from myrcene oxidation has been reported elsewhere, with a yield, corrected for secondary reactions

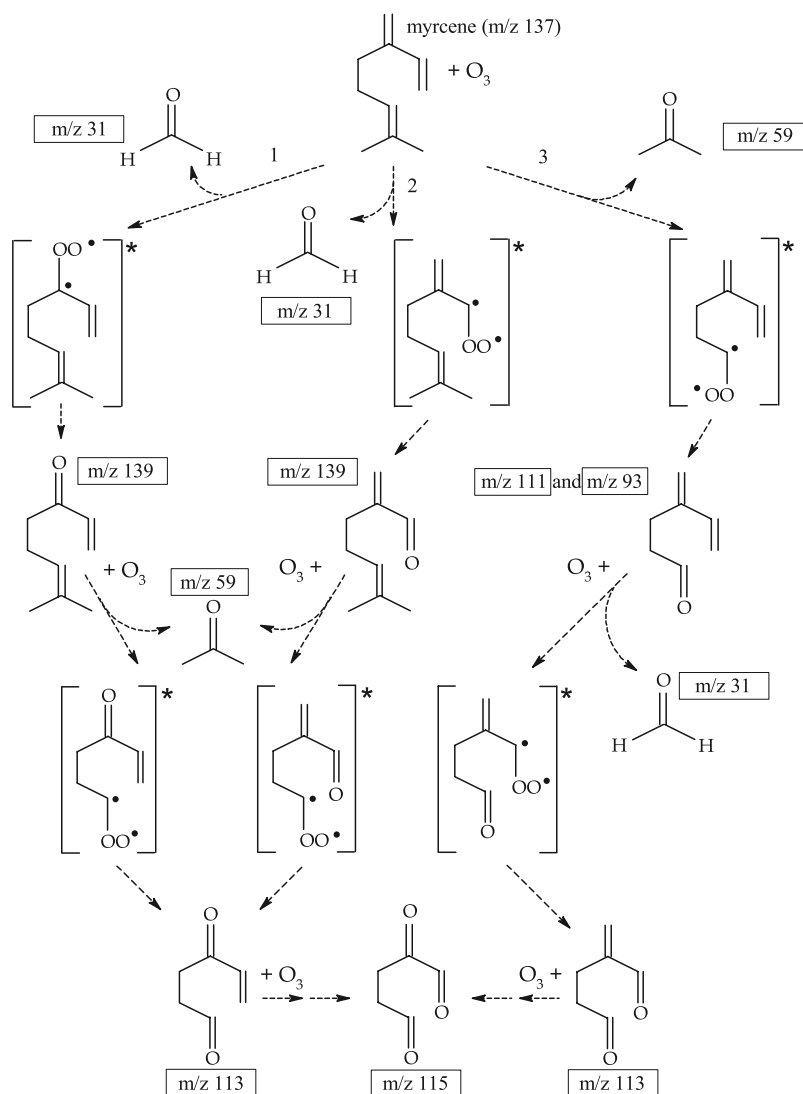


Figure 6. Partial mechanisms and proposed structures of selected oxidation products observed from myrcene ozonolysis. All boxed product ions were observed by PTR-MS. Dotted arrows represent multistep processes that, for clarity, are not illustrated here. Many other product ions were formed (Table 1), but we focus on the dominant products or products observed in ambient air by *Holzinger et al.* [2005].

with ozone, of $70 \pm 13\%$ [Reissell *et al.*, 2002], and corresponds to the structure proposed for m/z 111 + 93 in Figure 6. Corrections for the reactions of 4-vinyl-4-pentenal with ozone [Atkinson *et al.*, 1982] increased our calculated yield by 2%, however, because the rate constant of 4-vinyl-4-pentenal with ozone is assumed and not known, we do not apply this small correction to any of our data. The concentrations of m/z 111 + 93 are significantly higher than of m/z 139, suggesting that the dominant oxidation pathway is ozone attack at the double bond between carbons 6 and 7 (following pathway 3 in Figure 6). Acetone is formed more quickly than m/z 111 + 93 suggesting that the formation of acetone and the C_7 -CI from the POZ (Figure 6, pathway 3) dominates over the formation of a C_3 -CI and 4-vinyl-4-pentenal. 4-vinyl-4-pentenal can be formed from two pathways: the stabilization of the C_7 -CI (Figure 6), and as the primary carbonyl partner in the formation of the C_3 -CI (alternative CI from pathway 3 in

Figure 6, not shown). However, an OH yield from myrcene has been reported to be 0.63 [Aschmann *et al.*, 2002], suggesting that the hydroperoxide channel may be favored over stabilization for most of the Criegee intermediates, potentially resulting in less formation of 4-vinyl-4-pentenal from the C_7 -CI. Formaldehyde is formed later than acetone and other product ions (Figure 3), suggesting that it is formed from the ozonolysis of first-generation oxidation products. Although Figure 3a does not indicate m/z 113 undergoes further oxidation as suggested in Figure 6, the comparatively short timescale of this particular experiment likely prevented our observation of m/z 113 oxidation. Because m/z 115 was observed coincident with m/z 113, but at much lower concentrations (Figure 3a), the compound observed at m/z 115 likely does not come directly from the oxidation of m/z 113, but from a different, nondominant pathway. Other ions, m/z 73 and 75, are also formed quickly, but unlike m/z 111 and 93, do not decrease over the course

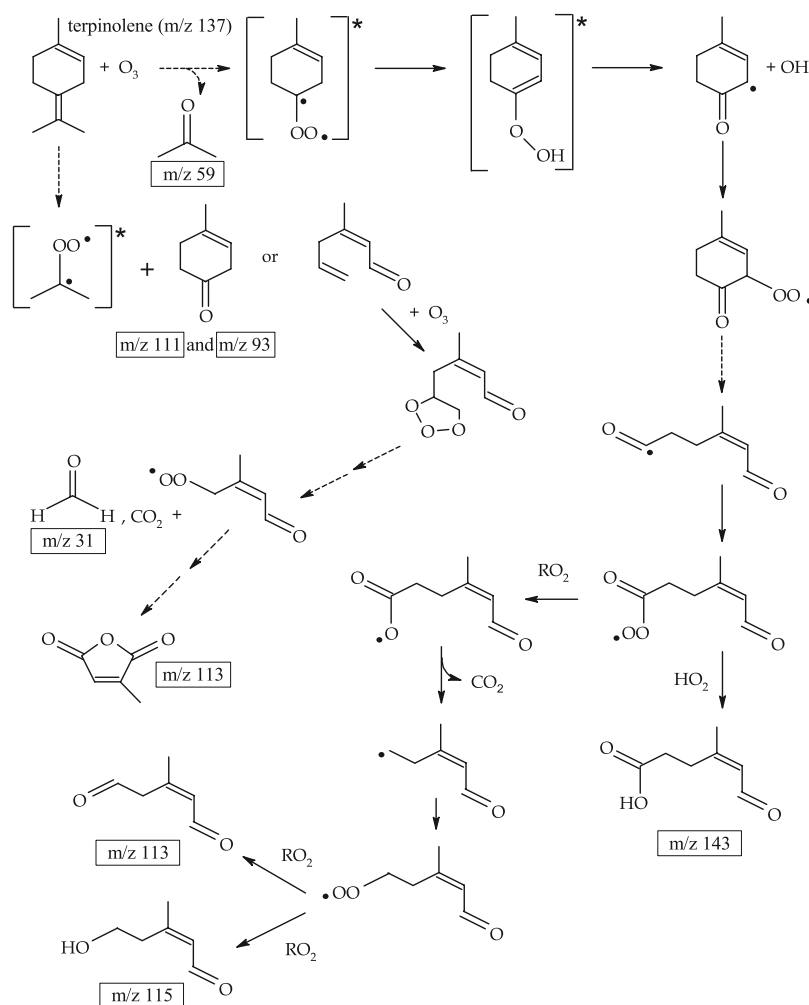


Figure 7. Partial mechanisms for the production of selected oxidation product ions from the ozonolysis of terpinolene. Additional Criegee intermediates and reaction pathways are possible but for clarity are not illustrated here.

of the experiment (Figure 3b). The concentrations of these product ions are significant, reaching 12–20 ppb, but oxidation products from the ozonolysis of myrcene with molecular weights of 72 and 74 amu are not readily determined.

3.4.2. Terpinolene

[30] Figure 4a shows that, like myrcene, ozonolysis of terpinolene produces ions occurring at m/z 111 and 93 that exhibit similar time structures ($R^2 = 0.99$), suggesting again that m/z 93 is the dehydrated fragment of m/z 111. The product 4-methyl-3-cyclohexen-1-one (MW = 110) has been identified from terpinolene oxidation [Hakola *et al.*, 1994]. The similar time series (Figure 4a) and yields of 4-methyl-3-cyclohexen-1-one ($53 \pm 9\%$) and acetone ($44 \pm 4\%$) suggest that acetone is only formed with 4-methyl-3-cyclohexen-1-one. The concentration of m/z 143 is low and highly variable (Figure 4a), suggesting that numerous other products resulted from the C_7 -CI. The initial increase in concentration of m/z 113, from 0.2 to 0.6 hours, occurred more slowly than the increase of m/z 111 and 93, remained level from 0.6 to 1.2 hours, then increased again after 1.2 hours, suggesting that different oxidation

products from terpinolene ozonolysis share the same m/z , but were formed at different times. The first increase in m/z 113 may have resulted from the direct ozonolysis of terpinolene, while the second increase in m/z 113 may have resulted from further oxidation of m/z 111 (Figure 7). Potential structures for these product ions from Figure 4a are shown in Figure 7. Figure 4b shows that m/z 93, 109 and 127 all reach their maximum concentrations when terpinolene is fully consumed, but m/z 109 and 127 do not decrease over the course of the experiment. In contrast, m/z 115 continues to increase after all the terpinolene has been consumed. Although m/z 115 and 113 are fairly well correlated ($R^2 = 0.94$), m/z 115 does not show the same initial peak in mixing ratio at ~ 0.6 hours as m/z 113, possibly suggesting that one of the products contributing to m/z 113 is formed through a similar pathway as m/z 115 (Figure 7), whereas the other product is formed more quickly through a different pathway.

3.4.3. α -terpinene

[31] Numerous product ions were observed from α -terpinene ozonolysis (Table 1). Figure 5 shows that α -terpinene is rapidly oxidized (within 30 min), and many product ions

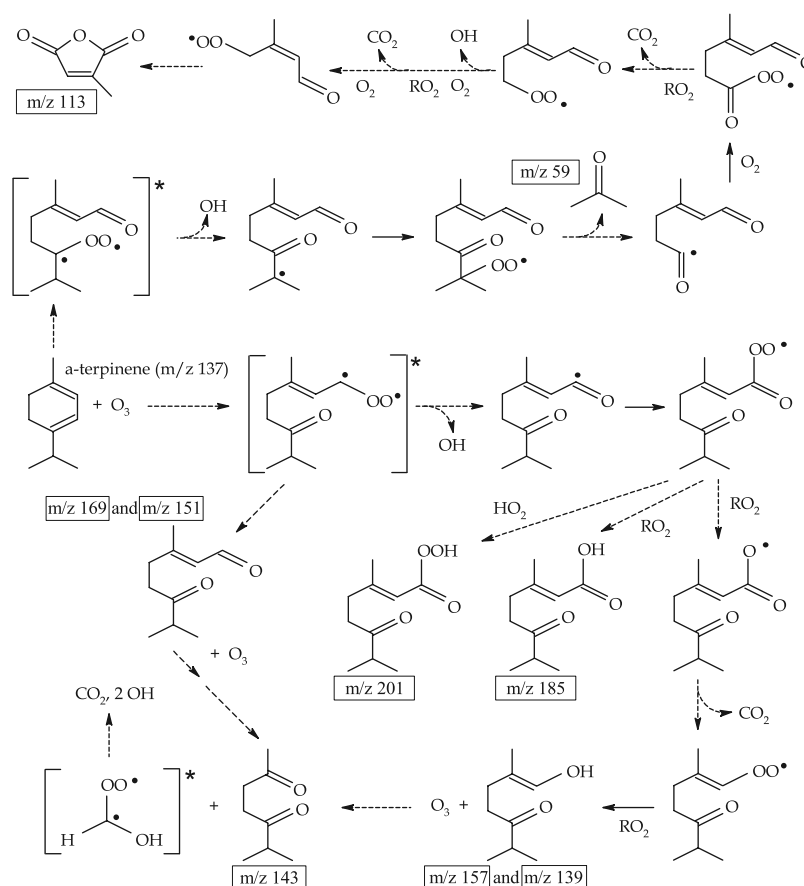


Figure 8. Partial mechanism for the ozonolysis of α -terpinene. Other possibilities for Criegee intermediates and reaction pathways exist but are not shown here.

are formed at low concentrations. Oxidation of α -terpinene is considerably more complicated than myrcene or terpinolene. The highest observed yield of a single ion occurred on m/z 139, with a yield of only $5.9 \pm 1.4\%$. With its two endo double bonds, the ozonolysis of α -terpinene should result in high yields of first generation products and produce low yields of second generation products. However, no product ions were observed at high yields, nor did any of the products, except m/z 139 which decreased by 50% in ~ 2 hours, decrease over the course of the 3.5 hour experiment, suggesting that the dominant first generation products were not detected, and that the observed product ions were likely second generation. Given its endo-double bonds, α -terpinene might be expected to initially form a keto-aldehyde, analogous to pinonaldehyde from α -pinene, that retains one double bond and occurs predominantly at m/z 169 and 151. In fact, m/z 169 and 151 were observed, but they continued to increase in concentration after all the α -terpinene was consumed, and did not decrease over the course of the experiment, suggesting that the observed m/z 169 and 151 were not product ions of “ α -terpinaldehyde”.

[32] Many different Criegee intermediates can be formed from α -terpinene, however, for simplicity we only illustrate three possibilities in Figure 8. In elucidating a mechanism for the formation of m/z 139 that retains a double bond, we could only find a compound occurring at m/z 139 as a

dehydrated fragment of m/z 157, which was observed, but not coincident with m/z 139. M/z 143 can be formed through different pathways from numerous other compounds (e.g., m/z 139, 169, 185, 201), but these secondary formation pathways for m/z 143 are not supported by the time series data. Simultaneous ozonolysis of the conjugated double bonds would form m/z 143 rapidly; however, the formation of a double POZ seems unlikely. The yields of all the gas-phase oxidation product ions are relatively low ($<10\%$), which is consistent with the high SOA yield observed from α -terpinene (Table 2). The observation of m/z 201 was particularly interesting because of its appearance after complete consumption of α -terpinene, and because of its high molecular weight which suggests it may participate in gas-to-particle partitioning. A structure for m/z 205 is suggested in Figure 8, however, the time evolution of m/z 201 and 185 suggest that they are not formed simultaneously, with the observation of m/z 201 occurring nearly one hour after m/z 185. A product occurring at m/z 113 was also observed (Figure 5a) at low concentrations (Table 5). The structure and formation mechanism for this compound is proposed in Figure 8, and is the same structure proposed for m/z 113 from terpinolene ozonolysis. The short lifetime of α -terpinene, its conjugated structure, its high SOA yield, and its production of numerous ions, many of which were observed in the forested atmosphere [Holzinger *et al.*, 2005], without straightforward formation mechanisms,

makes α -terpinene a particularly interesting and relevant monoterpene compound for further study.

4. Conclusions

[33] We conducted ozonolysis experiments on ten different terpene species to measure the time evolution and yields of gas-phase oxidation products and secondary organic aerosol. Yields of formaldehyde, acetone, and a few higher molecular weight oxidation products, such as nopinone, pinonaldehyde, and related acids, have been reported in the literature for a limited number of terpenes, and generally are in good agreement with the yields obtained from our experiments. Yields of SOA are also in good agreement with those reported elsewhere from experiments under similar experimental conditions. In addition to yields of previously reported compounds, we report yields of formaldehyde, acetaldehyde, formic acid, acetone, acetic acid, nopinone, α -pinene oxide, pinonaldehyde, and numerous other identified and unidentified compounds characterized by their mass to charge ratio, for the entire suite of ten terpene compounds. It is well known that the oxidation of any compound involves multiple steps, and the use of the PTR-MS in these experiments showed, in real time, the evolution of the different ions as first and second generation oxidation products.

[34] The PTR-MS is emerging as an important tool for the measurement of primary and secondary gas-phase compounds in field campaigns. Mass scans of ambient air will undoubtedly measure unidentified compounds, and concurrent or prior measurements of primary emissions at the given site will aid in narrowing the possible identities of the observed ions. Our results confirm that the product ions observed by *Holzinger et al.* [2005] are consistent with terpene ozonolysis reactions. Observations of unidentified products [*Holzinger et al.*, 2005] and knowledge of primary emissions [*Lee et al.*, 2005], together with the results reported here of the identified, tentatively identified, and unidentified oxidation products from primary terpene compounds, aid greatly in understanding the magnitude and significance of within-canopy oxidation. Because the detection of very reactive parent terpene emissions is difficult in ambient air, observations of the ions described in this study can serve as markers for within-canopy chemistry and reactivity. Thus these product ions are likely to be of significant interest to scientists conducting field measurements in atmospheric chemistry, biosphere-atmosphere exchange of volatile organic compounds, and secondary organic aerosol composition. Further experiments to identify the compounds contributing to the unidentified products are necessary and will be more useful to laboratory chemists and kineticists for the elucidation of more complete terpene oxidation mechanisms.

[35] In the real atmosphere, while ozonolysis may be the dominant loss process for some terpenes (i.e., α -terpinene, terpinolene, myrcene, β -caryophyllene, and α -humulene), photo-oxidation may dominate the loss of other terpenes. Thus, to accurately assess the impacts and gas-phase products of terpenes, photo-oxidation experiments were also performed and will be reported elsewhere (A. Lee et al., Gas-phase products and secondary aerosol yields from the photo-oxidation of sixteen different terpenes, submitted to

Journal of Geophysical Research, 2006). The results from both the ozonolysis and photo-oxidation experiments can be used in future modeling efforts and field campaigns to better constrain the contribution of biogenic compounds to SOA production and their impacts on the oxidative capacity of the atmosphere, and to detect the photochemical signatures from emissions of very reactive biogenic VOCs.

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