

Effect of Relative Humidity on the Chemical Composition of Secondary Organic Aerosol Formed from Reactions of 1-Tetradecene and O₃

HERBERT J. TOBIAS,[†]
KENNETH S. DOCHERTY,[‡]
DEREK E. BEVING,[‡] AND
PAUL J. ZIEMANN^{*,§}

Air Pollution Research Center, Department of Environmental Sciences, and Environmental Toxicology Graduate Program, University of California, Riverside, California 92521

The chemical composition of secondary organic aerosol formed in an environmental chamber from ozonolysis of 1-tetradecene in humid and dry air was determined using a thermal desorption particle beam mass spectrometer (TDPBMS). The major products are α -hydroxytridecyl hydroperoxide and bis(α -hydroxytridecyl) peroxide in humid air and symmetric C₂₆ and asymmetric C₁₄ secondary ozonides in dry air. The hydroperoxide is formed by reaction of stabilized Criegee biradicals with water vapor, and the peroxide (a peroxyhemiacetal) is formed by subsequent reaction of the hydroperoxide with tridecanal. The secondary ozonides are formed by reactions of stabilized Criegee biradicals with tridecanal and formaldehyde. Tridecanoic acid was also observed in both experiments. These compounds have very low vapor pressures and are stable on the 3-h time scale of the environmental chamber experiments. When collected aerosol was analyzed by gas chromatography, the hydroperoxides, peroxides, and secondary ozonides thermally decomposed to more volatile compounds, including tridecanal, tridecanoic acid, and a few unidentified products.

Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere from a variety of anthropogenic and biogenic sources (1, 2). There they undergo photochemical reactions with O₃, OH, and NO₃ (3, 4) that may lead to low-volatility products that subsequently become incorporated into aerosol particles (5) and contribute to fine (<2.5 μ m diameter, PM-2.5) particulate organic mass. For example, organics typically constitute ~20–50% of the mass of fine particles in the continental United States (6) and ~30% in southern California, with ~20–30% of that amount being generated by secondary processes (7). During smog episodes, secondary organic aerosol can apparently contribute up to ~80% of the organic particulate matter in Los Angeles (8, 9). Information on secondary organic aerosol composition and the mechanisms by which this material is formed is relatively scarce,

but in recent years has become more available through environmental chamber investigations of VOC photooxidation reactions (10–16). Such studies are important for understanding the formation and fate of the secondary organic component of the atmospheric aerosol and for developing models that accurately describe these processes (12, 17, 18).

The primary analytical tool used to identify organic aerosol compounds has been gas chromatography–mass spectrometry (GC-MS). The technique is typically applied to samples collected on filters or by impaction, which are then extracted in solvent and sometimes derivatized prior to GC-MS analysis. Although this is a powerful approach, it is known that the sampling procedures can introduce artifacts due to adsorption/desorption of vapors (19, 20) and contamination due to handling and analytical workup. Recently developed denuders are helping to reduce sampling problems (16, 18). Other problems arise because gas chromatography of polar compounds often requires derivatization, which adds time and complexity to analyses, and labile compounds can decompose or polymerize on a GC column, during solvent extraction or during derivatization.

We have recently begun to investigate the chemistry of secondary organic aerosol formation using a thermal desorption particle beam mass spectrometer (TDPBMS) we developed for online analysis of aerosol composition. The instrument can be used to obtain total-particle mass spectra in real-time by impacting particles on a hot surface, which rapidly desorbs all compounds for simultaneous mass analysis (21). Individual compound mass spectra can be obtained by cryogenically collecting and then slowly heating particles to temporally separate compounds according to volatility (22). The TDPBMS technique offers advantages over GC-MS, in that real-time information can be obtained, analytical artifacts are reduced because of less sample handling, and alteration of labile compounds is less likely because vaporization occurs more rapidly, at lower temperatures, and in a vacuum. To date, TDPBMS has been used to analyze the chemical composition of secondary organic aerosol formed from ozonolysis of 1-tetradecene, which serves as a surrogate compound for the normal alkenes. Elsewhere in this issue (23) we describe studies that have identified α -alkoxytridecyl and α -acyloxytridecyl hydroperoxides as the major aerosol products of reactions occurring in dry air in the presence of excess alcohol or carboxylic acid vapor, which is consistent with the Criegee reaction mechanism of ozonolysis (24). It is also shown there that these compounds subsequently react with aldehydes, apparently on particle surfaces, to form peroxyhemiacetals.

Although compounds containing various functional groups have been identified in aerosol, there have been few reports (25–27) of hydroperoxides or peroxides, and none have been observed using GC-MS for analysis. It is well-known that organic hydroperoxides and peroxides are formed during liquid-phase ozonolysis of alkenes in organic (24) and aqueous solutions (26, 27), and they have been identified in precipitation (28). Hydroperoxides have also been observed as volatile products from the gas-phase ozonolysis of ethene (29–32). Hydroperoxides and peroxides have been of interest for some time because of their activity as atmospheric oxidants, and this same property has made them of current interest as a potential causative agent for the adverse effects of fine particles on human health (33, 34). In our previous work we began to investigate the potential importance of these compounds in aerosol nucleation and growth, and we continue here with a report on the aerosol products formed

* Corresponding author phone: (909)787-5127; fax: (909)787-5004; e-mail: paul.ziemann@ucr.edu.

[†] Air Pollution Research Center.

[‡] Air Pollution Research Center and Environmental Toxicology Graduate Program.

[§] Air Pollution Research Center, Department of Environmental Sciences, and Environmental Toxicology Graduate Program.

from reactions of 1-tetradecene and O₃ in dry and humid air in the absence of added alcohols and carboxylic acids. These experiments more nearly approximate the range of conditions encountered in the ambient atmosphere, and the results provide further insight into the aerosol chemistry of alkene-O₃ reactions and also allow a comparison of the TDPBMS technique with GC-MS.

Experimental Section

Materials. Fine chemicals were obtained from Aldrich Chemical, Inc., and were used without further purification. All solvents were HPLC grade, obtained from Fisher.

Aerosol Mass Spectrometric Analysis by TDPBMS and TPTD. Detailed descriptions of the TDPBMS and its operation for real-time analysis (21) and temperature-programmed thermal desorption (TPTD) (22) are presented elsewhere. Aerosol was sampled into the TDPBMS through a 100 μ m orifice, which maintains the flow at 0.075 L/min and reduces the pressure from atmospheric to 2 Torr. Particles then enter a tube containing a series of aerodynamic lenses (35, 36), which focus the particles into a very narrow, low-divergence particle beam that transports ~ 0.02 – 0.5 μ m particles from atmospheric pressure into the high-vacuum chamber with near-unit efficiency. After exiting the aerodynamic lens nozzle, particles pass through two flat-plate skimmers separating three differentially pumped chambers and enter the detection chamber where the pressure is 5×10^{-8} Torr. The vacuum is maintained by turbomolecular pumps mounted on each chamber and backed by an oil-free mechanical pump to reduce contaminating organic vapors in the system. Inside the detection chamber particles impact on the walls of a V-shaped molybdenum foil that is either resistively heated continuously at 165 ± 3 °C for real-time TDPBMS analysis or cooled to -50 °C by an external liquid nitrogen bath for collection of particles for TPTD. The vaporizer temperature is monitored by an attached thermocouple and during real-time analysis is regulated by a temperature controller. After vaporization the molecules diffuse into an ionizer where they are impacted by 70 eV electrons, and the resulting ions are mass analyzed in a quadrupole mass spectrometer (Extrel MEXM 500, 1–500 amu mass range) equipped with a conversion dynode/pulse counting detector.

Particle analysis by TPTD was carried out on ~ 1 μ g of aerosol collected in ~ 30 min on the cryogenically cooled vaporizer. The sample was desorbed by heating at a ramp rate of ~ 1 °C/min for ~ 2 h, while mass spectra were continuously recorded. During TPTD the aerosol components desorb according to their vapor pressures, so mass spectra of individual compounds can be extracted from the time-dependent mass spectra. Although this technique is primarily used to identify major aerosol components, we have demonstrated (22) that for sufficiently large differences in vapor pressures it is possible to obtain mass spectra for compounds present at concentrations at least an order of magnitude less than those of the major components.

Because particles are exposed to subsaturated air when sampling from the DMA (calibration particles) and within the TDPBMS vacuum (calibration and chamber particles), volatile compounds may evaporate prior to analysis. Calculations and experiments with compounds of known vapor pressures (21) indicate that significant evaporation can occur for calibration particles with vapor pressures greater than $\sim 10^{-5}$ Torr, but that environmental chamber particles probably require higher vapor pressures, since they are exposed to subsaturated conditions for a shorter period during sampling. This is not expected to pose a serious problem for the TDPBMS technique, however, since gas-particle partitioning calculations and measurements (37) indicate that in the ambient atmosphere compounds with

vapor pressures greater than $\sim 10^{-5}$ Torr will be present primarily ($>90\%$) in the gas phase. A greater fraction of semivolatile compounds can reside in particles at the higher mass concentrations obtained in environmental chamber experiments, but loss of these compounds during sampling will not lead to artifacts regarding the identity of compounds that would actually reside in ambient particles.

Generation of Aerosol Standards for TDPBMS. As an aid in identifying environmental chamber aerosol components, two secondary ozonides (see ozonides I and II below for structures) were synthesized by liquid-phase ozonolysis of 1-tetradecene in hexane and analyzed by TPTD. The liquid-phase reaction is known to give high yields of these compounds (38). The ozonides were prepared by dissolving 1.5 mL of 1-tetradecene in 25 mL of hexane and then bubbling $\sim 2\%$ O₃/O₂ from a Welsbach T-408 O₃ generator through a dry ice-cooled solution at 1.5 L/min for 5 min, which was sufficiently long to react nearly all the alkene without adding much excess O₃. The secondary ozonides were separated from other components by flash chromatography (39) using a 1.2:1 ethyl ether/hexane solvent mixture and identified by reacting with iodide on TLC plates (40). The separated fraction containing the secondary ozonides was atomized using a Collision atomizer with dry, clean air as the carrier gas. The aerosol from the atomizer passes through diffusion driers containing activated charcoal to adsorb the solvent, leaving a submicrometer-sized aerosol of the low-volatility solutes. The particles are then charged to near-Boltzmann equilibrium (41) as they pass through a radioactive bipolar charger containing ²¹⁰Po, and the polydisperse, charged aerosol enters a differential mobility analyzer (DMA) (42) for selection of a monodisperse aerosol, which enters the TDPBMS. The particles we used had diameters of 0.2 μ m. TPTD provided the final stage of separation of the two ozonides prior to mass spectrometric analysis. A standard of α -hydroperoxy-tridecyl tridecanoate was prepared, purified, and analyzed using the same techniques, with the exception that 3 g of tridecanoic acid was added to the 1-tetradecene/hexane solution prior to ozonolysis, and the reaction was carried out at room temperature. This procedure gives high yields of α -acyloxyalkyl hydroperoxides (43).

Environmental Chamber Technique. Secondary organic aerosol was formed in a series of environmental chamber experiments from reactions of 1-tetradecene and O₃ in humid and dry air. Aerosol was generated by reacting 0.5 ppmv of 1-tetradecene (92% purity) with 1.5 ppmv of O₃ in a 7000 L Teflon bag at room temperature (~ 23 °C). For the dry-air experiments the chamber was filled with clean air (<5 ppbv hydrocarbons) from an Aadco pure air generator, which according to the manufacturer has a relative humidity (RH) of 0.1%. For the humid-air experiments an RH of 30% was achieved by adding water vapor to the clean air. The RH was measured using a Vaisala HMP230 probe, which has an accuracy of $\pm 1\%$ RH. In the dry-air experiments the reading was zero, so the RH should have been less than 1% and was probably close to 0.1%. In all experiments 1000 ppmv of cyclohexane was added to the chamber to scavenge $>95\%$ of the OH radicals formed in the alkene-O₃ reaction (44). The 1-tetradecene, cyclohexane, and water were added to the chamber by evaporating the heated liquids from a glass bulb into a clean air stream. In one humid-air experiment ~ 10 ppmv of formaldehyde was added to the chamber prior to the start of the ozonolysis reaction. Formaldehyde was obtained by evaporating paraformaldehyde into a glass bulb at a measured pressure and then flushing into the chamber using clean air. In another experiment ~ 25 ppmv of pentanal was added to the chamber by the same method. Ozone was added to the chamber last by flowing clean air through a 0.5 L bulb containing $\sim 2\%$ O₃/O₂. During all chemical additions a fan was run to mix the chamber and was then turned off.

Aerosol was formed by homogeneous nucleation, usually a few minutes after adding O_3 , and was sampled directly into the TDPBMS through stainless steel tubing inserted into a port in the chamber wall. Particles were either analyzed in real time or by TPTD. It is possible to obtain size-dependent composition information by sampling the aerosol through a DMA and then into the TDPBMS, but this was not done here. In some experiments aerosol size distributions were measured using a scanning electrical mobility spectrometer (21, 45). Particle concentrations after addition of 1-tetradecene were less than $10/cm^3$ and then typically reached $\sim 10^4$ – $10^6/cm^3$ a few minutes after addition of O_3 . Within about an hour, which is the approximate lifetime of 1-tetradecene at this O_3 concentration (the lifetime of 1-tetradecene due to reaction with 1.5 ppmv of O_3 is ~ 50 min, estimated using a 1-decene rate constant of $9.3 \times 10^{-18} cm^3/molecule \cdot s$ (4)), relatively constant size distributions were achieved, with average particle diameters of ~ 0.2 – $0.4 \mu m$ and mass concentrations of ~ 500 – $2000 \mu g/m^3$. Aerosol wall losses were $\sim 20\%/h$ over the 1–3 h experiments. Detection limits for real-time TDPBMS analysis are ~ 0.1 – $1 \mu g/m^3$, so the amount of aerosol formed was much more than is needed for those measurements. The high concentrations were used to reduce sampling times for TPTD and to obtain high signal-to-noise, especially for detection of minor components during real-time analysis. Background contributions to mass spectra were negligible except for m/z 28, 32, 40, and 44 (N_2^+ , O_2^+ , Ar^+ , and CO_2^+ , respectively), and so only contributions from these masses were subtracted from the mass spectra. Ozone concentrations were measured by drawing chamber air through Teflon tubing into a Dasibi 1003-AH O_3 analyzer. After each experiment the chamber was pumped out and then refilled and flushed until the following day or longer (> 10 chamber volumes). Occasionally DOS particles (dioctyl sebacate, a low volatility organic ester) were added to the flushed chamber to ascertain the presence of low volatility contaminant vapors that could partition into particles during chamber studies, but no contaminants were observed.

Aerosol Collection and Gas Chromatographic Analysis.

Aerosol for gas chromatographic analysis was collected using a MOUDI (microorifice uniform deposit impactor) sampler (46). The impaction substrates were aluminum foil and were cleaned by baking at $350^\circ C$ for 12 h. After sampling 1800 L of chamber air through the MOUDI, the substrates from the lowest six stages (0.056 – $1.0 \mu m$ cut size, no after-filter) were pooled and extracted using dichloromethane. The extract was concentrated to 1 mL and spiked with pentadecane as an internal standard. Samples were injected at $150^\circ C$ into a split/splitless injector, excess solvent was purged, and the sample was cryo-focused onto a 30 m, 0.53 mm ID, DB-1701 column in a Hewlett-Packard 5970 GC equipped with a flame ionization detector. The column was initially held at $40^\circ C$ for 2 min and then ramped to $280^\circ C$ at $10^\circ C/min$. Tridecanal and tridecanoic acid were identified and quantified by comparing retention times and peak areas with those of standard compounds, and unknown compound concentrations were estimated using an assumed FID response factor. Identification was verified by GC-MS analysis on a Varian 3400/2000 gas chromatograph/ion trap mass spectrometer using a similar column and procedure as for the GC-FID analysis.

Results and Discussion

TPTD Analysis of Aerosol Products Formed from Ozonolysis of 1-Tetradecene in Humid Air. The results of TPTD analysis of aerosol formed from reaction of 1-tetradecene [$CH_3(CH_2)_{11}CH=CH_2$] and O_3 in air at 30% relative humidity are shown in Figures 1 and 2. An example of a “mass thermogram”, which is a plot of the signal intensity vs vaporizer temperature for a particular m/z (mass/charge) ratio, is shown in Figure

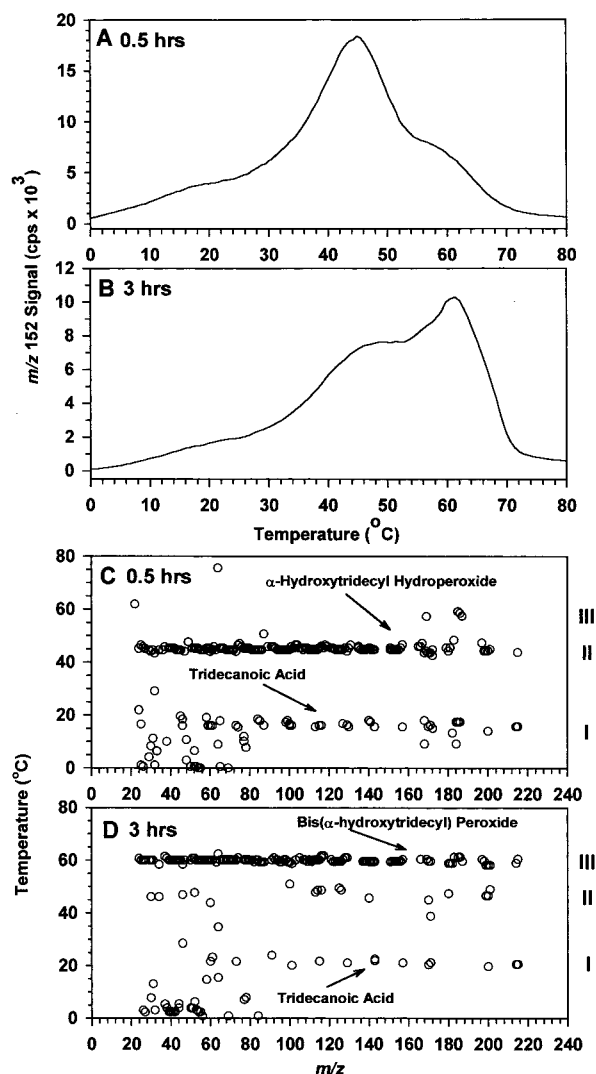


FIGURE 1. Mass thermograms for m/z 152 for aerosol collected after (A) 0.5 h and (B) 3 h, and differential mass thermograms for aerosol collected after (C) 0.5 h and (D) 3 h. The aerosol was formed from ozonolysis of 1-tetradecene in air with 30% relative humidity. The three product compounds are labeled I, II, and III.

1A for m/z 152 for aerosol collected after 0.5 h of reaction. The desorption profile has a single maximum at $\sim 46^\circ C$ and shoulders at $\sim 20^\circ C$ and $\sim 61^\circ C$. The temperatures assigned to the shoulders were determined from other m/z plots where they appear as maxima. Each of the three features in the mass thermogram corresponds to a different compound, with the most volatile one appearing first. After 3 h the $61^\circ C$ feature in the m/z 152 plot becomes a maximum, and shoulders are present at $20^\circ C$ and $46^\circ C$ (Figure 1B). The shifts in the relative intensities of the features between 0.5 and 3 h are indicative of changes in the relative abundances of the aerosol components, but the small shifts in the desorption temperatures are not significant, since they depend slightly on the sample size and the temperature ramp rate. We designate these compounds according to their desorption temperatures as I ($20^\circ C$), II ($46^\circ C$), and III ($61^\circ C$). Thermograms can be produced for other m/z ratios and used to generate a “differential mass thermogram”, which is a plot of the temperatures at which signal maxima occur (i.e. the “desorption temperatures”) for each m/z . In this type of plot each compound produces a horizontal band of points that appears at the compound’s desorption temperature. Differential mass thermograms for aerosol collected after 0.5 and 3 h are shown in Figure 1C,D, and exhibit bands

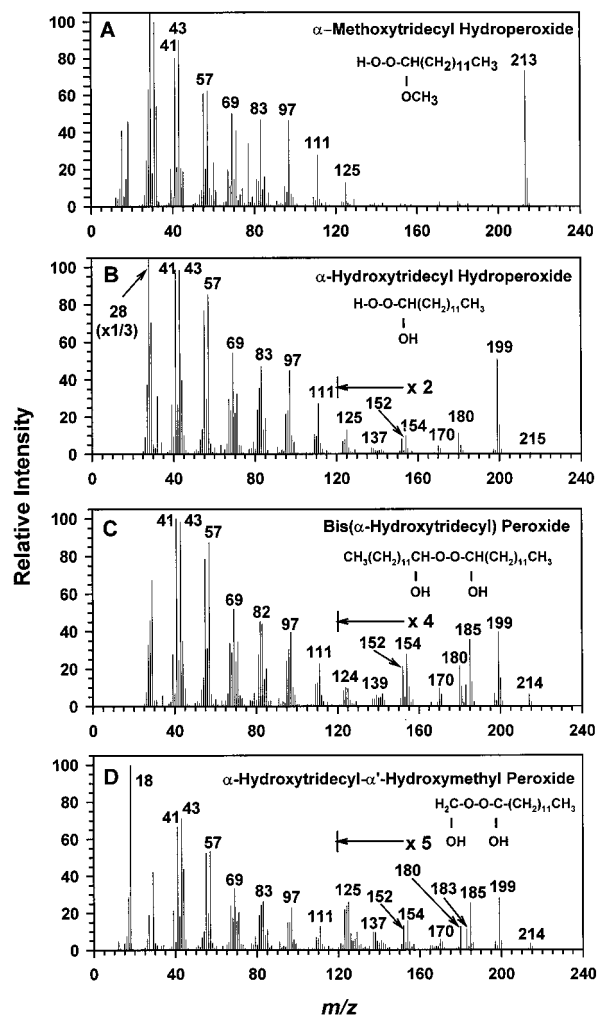


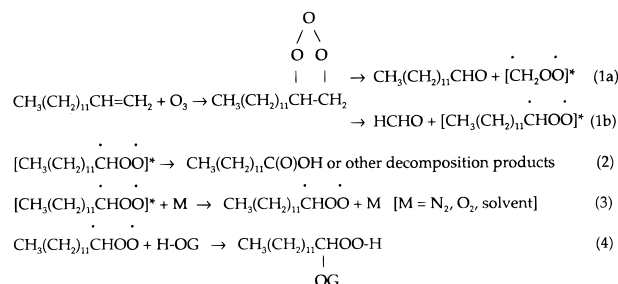
FIGURE 2. Mass spectra of (A) α -methoxytridecyl hydroperoxide obtained by real-time TDPBMS analysis of a synthesized standard and (B) α -hydroxytridecyl hydroperoxide, (C) bis(α -hydroxytridecyl) peroxide, and (D) α -hydroxytridecyl- α' -hydroxymethyl peroxide obtained by TPTD analysis of aerosol formed from ozonolysis of 1-tetradecene in air with 30% relative humidity (and added formaldehyde for D). Mass spectrum B was obtained from the data shown in Figure 1C for compound II, and mass spectrum C was obtained from the data shown in Figure 1D for compound III.

corresponding to compounds I, II, and III. The points that appear below compound I at ~ 0 – 10 $^{\circ}\text{C}$ are due to cyclohexane, the OH scavenger, which is present in the environmental chamber at such a high concentration (1000 ppmv) that some of the vapor reaches the detection chamber of the TDPBMS and adsorbs onto the cooled vaporizer. Cyclohexane and its OH reaction products do not participate in aerosol formation since the cyclohexane is nonreactive, and the product concentrations are too low to compete with other compounds in reactions with stabilized biradicals. More data points are obtained when a compound is present in high relative abundance (0.5 h for compound II and 3 h for compound III), because more maxima appear in the mass thermograms and these are easier for our software to identify than shoulders. The scatter is due to uncertainty in determining the location of maxima and shoulders. A mass spectrum of each compound can be obtained by plotting the maximum signal intensity for each mass in a desorption band. The mass spectrum of compound I is not shown but matches that of tridecanoic acid [$\text{CH}_3(\text{CH}_2)_{11}\text{C}(\text{O})\text{OH}$]. The mass spectrum of α -methoxytridecyl hydroperoxide [$\text{CH}_3(\text{CH}_2)_{11}\text{-CH}(\text{OCH}_3)\text{OOH}$] from our previous study (23) is shown in

Figure 2A, and the mass spectrum of compound II at 0.5 h is shown in Figure 2B. Based on a comparison of these spectra, and in accordance with the products expected to be formed by the Criegee mechanism of alkene ozonolysis in the presence of acidic compounds (24), we propose that compound II is α -hydroxytridecyl hydroperoxide [$\text{CH}_3(\text{CH}_2)_{11}\text{CH}(\text{OH})\text{OOH}$], which is hereafter abbreviated as HTHP.

The m/z 199 peak in the HTHP mass spectrum is due to loss of HO_2 from the molecular ion. This is a characteristic fragmentation pathway for α -alkoxy and α -acyloxy alkyl hydroperoxides (23), as seen from the large m/z 213 peak in the mass spectrum of α -methoxytridecyl hydroperoxide (Figure 2A). The ion series corresponding to $\text{C}_n\text{H}_{2n-1}^+$ (27, 41, ..., 125) and $\text{C}_n\text{H}_{2n+1}^+$ (29, 43, ..., 113) are also characteristic of these compounds. In addition, the HTHP mass spectrum contains relatively intense peaks at m/z 137, 138, 152, 154, 170, and 180, which are also prominent in the mass spectrum of tridecanal [$\text{CH}_3(\text{CH}_2)_{11}\text{CHO}$] (not shown). This suggests that one of the fragmentation pathways for HTHP may involve loss of H_2O_2 to form the tridecanal molecular ion, which then undergoes its normal fragmentation.

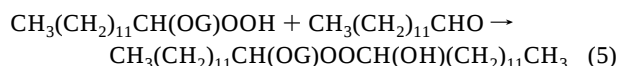
The mechanism of the reaction of 1-tetradecene and O₃ in the presence of acidic compounds, which is supported by liquid-phase studies on a variety of alkenes (24, 43, 47, 48), gas-phase studies on ethene (4, 29–32), and our previous TDPBMS analyses of aerosol formed from gas-phase and liquid-phase reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids (23), is shown below.



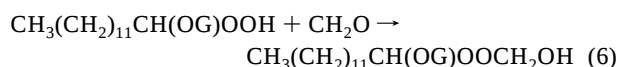
The reaction is initiated by addition of O_3 to the 1-tetradecene double-bond, resulting in the formation of a 1,2,3-trioxolane (primary ozonide). The energy-rich primary ozonide rapidly decomposes by cleavage of the terminal C—C bond and either of the O—O bonds to form tridecanal and a small excited Criegee biradical $[CH_2OO]^*$ (reaction 1a) and formaldehyde and a large excited Criegee biradical $[CH_3-(CH_2)_{11}CHOO]^*$ (reaction 1b). In the gas phase (4), the large biradical can undergo a number of possible unimolecular reactions that lead to a variety of products (reaction 2), including tridecanoic acid, dodecane, and hydroxycarbonyls generated through a channel that also leads to OH formation, or can be stabilized by collisions with other molecules (e.g. N_2 or O_2 for reactions in air) (reaction 3). The small biradical undergoes similar reactions (e.g. formic acid $[CH(O)OH]$ is formed as in reaction 2). Of the potential products of unimolecular biradical reactions only tridecanoic acid and some of the hydroxycarbonyls are likely to have sufficiently low vapor pressures to partition significantly into aerosol. The large stabilized biradical $CH_3(CH_2)_{11}CHOO$ can undergo reactions with species including SO_2 , CO, NO_2 , and aldehydes (49), but in the presence of sufficiently high concentrations of acidic compounds (H—OG), such as alcohols ($G = R =$ alkyl group), carboxylic acids ($G = C(O)R =$ acyl group), or water ($G = H$), the primary products are expected to be α -alkoxytridecyl, α -acyloxytridecyl, and α -hydroxytridecyl hydroperoxides, respectively (reaction 4) (24, 29, 30). Unless the alcohol or carboxylic acid is relatively large, reactions of

the small stabilized biradical $\dot{\text{C}}\text{H}_2\text{O}\dot{\text{O}}$ lead to products too volatile to partition into aerosol.

In our previous studies (23), formation of each α -alkoxytridecyl or α -acyloxytridecyl hydroperoxide was followed by the appearance of a less volatile compound that increased in abundance over time and had a mass spectrum similar to that of the corresponding hydroperoxide. In accordance with the known liquid-phase reaction between hydroperoxides and aldehydes (50–53), we proposed that the low-volatility compounds were peroxyhemiacetals formed by reaction of α -alkoxytridecyl or α -acyloxytridecyl hydroperoxides with tridecanal.



Also in those studies, when ~ 10 ppmv of formaldehyde was added to the chamber at the beginning of an experiment to increase the [formaldehyde]/[tridecanal] concentration ratio from ~ 1 to ~ 30 , reaction 5 was completely suppressed by reaction of the hydroperoxide with formaldehyde.



Based on these results, the expectation that the gas-phase reaction between these closed-shell species would be slow and gas-particle partitioning calculations which indicated that the [formaldehyde]/[tridecanal] ratio would be very small inside particles, it was concluded that reactions 5 and 6 apparently occurred on particle surfaces.

Similar reactions were observed here for HTHP. The TPTD mass spectrum of compound III is shown in Figure 2C. It is similar to that of HTHP (Figure 2B) except that in compound III m/z 82 and 124 are local signal maxima instead of 83 and 125, and strong peaks also appear at m/z 185 and 214. When formaldehyde was added to the chamber, compound III was replaced by a new compound IV that desorbed at $\sim 52^\circ\text{C}$, which is approximately midway between the desorption temperatures of compounds II and III. The mass spectrum of compound IV is shown in Figure 2D and is similar to that of compound III, except that m/z 83 and 125 are local signal maxima instead of m/z 82 and 124. From these results we conclude that compound III is bis(α -hydroxytridecyl) peroxide $[\text{CH}_3(\text{CH}_2)_{11}\text{CH}(\text{OH})\text{OOCH}(\text{OH})(\text{CH}_2)_{11}\text{CH}_3]$ and compound IV is α -hydroxytridecyl- α' -hydroxymethyl peroxide $[\text{CH}_3(\text{CH}_2)_{11}\text{CH}(\text{OH})\text{OOCH}_2\text{OH}]$, formed by reactions 5 and 6, respectively, where $\text{G} = \text{H}$.

TPTD Analysis of Aerosol Products Formed from Ozonolysis of 1-Tetradecene in Dry Air. From the chemistry described above, the most likely aerosol products formed from ozonolysis of 1-tetradecene in dry air in the absence of excess alcohol or carboxylic acid are tridecanoic acid (reaction 2), α -acyloxyalkyl hydroperoxides formed by reaction of tridecanoic or formic acid with stabilized biradicals (reaction 4), and peroxyhemiacetals formed by reaction of α -acyloxyalkyl hydroperoxides with tridecanal or formaldehyde (reactions 5 and 6). However, because of the low concentrations of acidic species it is also possible for tridecanal and formaldehyde to react with stabilized biradicals to form two relatively low-volatility secondary ozonides.

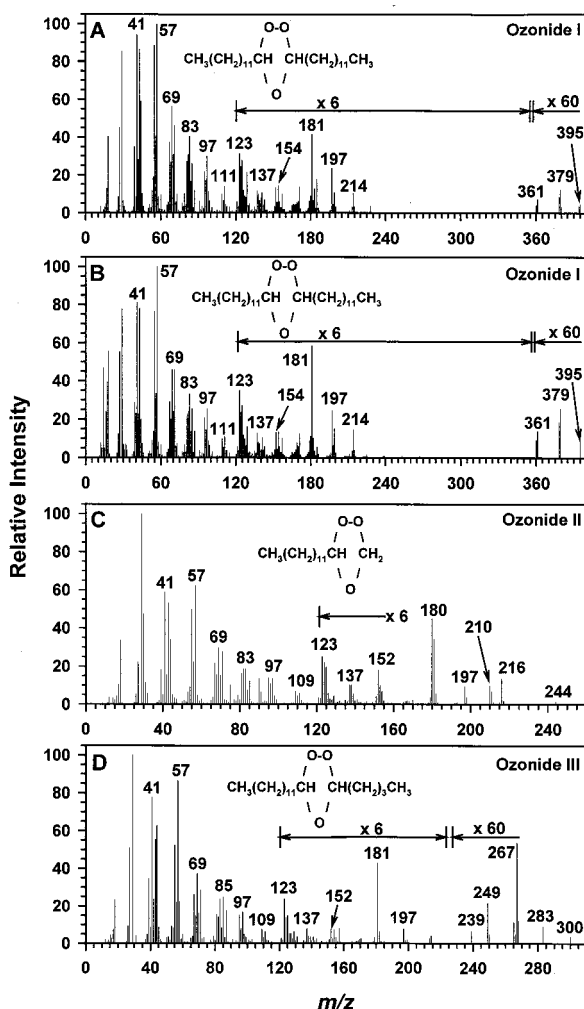
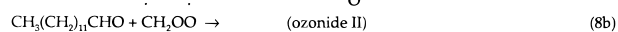
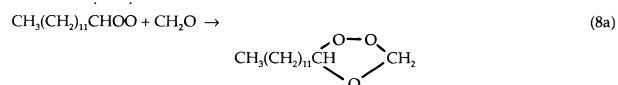
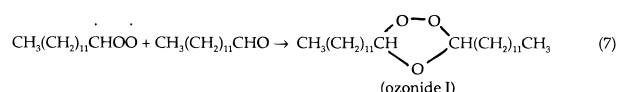


FIGURE 3. TPTD mass spectra of secondary ozonides in aerosol formed from ozonolysis of 1-tetradecene in (A) dry air, (B, C) liquid cyclohexane, and (D) air with 30% relative humidity and ~ 25 ppmv added pentanal.

A third secondary ozonide, formed by reaction of the small biradical with formaldehyde, would be too volatile to create aerosol. Secondary ozonides have been observed among the gas-phase products of ozonolysis of ethene (31, 54, 55) and 2-butene (56) in dry air and are the major products formed from liquid-phase ozonolysis of alkenes in nonreactive solvents such as alkanes (24, 38).

TPTD analysis of aerosol formed in dry air indicates the presence of three major compounds: tridecanoic acid and compounds that desorb at $\sim 70^\circ\text{C}$ and $\sim 88^\circ\text{C}$. The mass spectrum of the 70°C compound is shown in Figure 3A and can be identified as ozonide I by the near-perfect match with the mass spectrum of a standard of this compound, which is shown in Figure 3B. The standard was prepared by liquid-phase synthesis and desorbed at $\sim 60^\circ\text{C}$. The slightly higher desorption temperature of ozonide I from the chamber is probably due to a larger sample size and interactions with the 88°C compound. The mass spectrum of a synthesized ozonide II standard, which desorbs at $\sim 14^\circ\text{C}$, is shown in Figure 3C. There appeared to be only a trace of this compound in the chamber aerosol, probably because of its relatively high vapor pressure. From our correlation of vapor pressure and desorption temperature (23) we estimate vapor pressures at 25°C of $\sim 4 \times 10^{-11}$ Torr for ozonide I and $\sim 4 \times 10^{-4}$ Torr for ozonide II. We have observed particle evaporation during TDPBMS sampling for compounds having vapor pressures less than $\sim 10^{-5}$ Torr (21), so a significant amount of ozonide

II could evaporate from the aerosol before reaching the TDPBMS. The amount can be estimated by using gas-particle partitioning theory to calculate aerosol yields (12) from ozonides I and II. According to this approach, the gas-particle partition coefficient, K_i , in units of $\text{m}^3/\mu\text{g}$, for a compound i absorbed in a pure liquid organic particle is given by

$$K_i = C_{p,i}/C_{g,i}M_o = 760RT/MW_{om}10^6\zeta_i p_{L,i}^\circ \quad (9)$$

where $C_{p,i}$ is the concentration of i in particles in ng/m^3 , $C_{g,i}$ is the concentration of i in the gas phase in ng/m^3 , M_o is the particulate organic mass concentration in $\mu\text{g}/\text{m}^3$, R is the ideal gas constant $= 8.206 \times 10^{-5} \text{ m}^3\text{-atm}/\text{mol}\cdot\text{K}$, T is the temperature in K, MW_{om} is the mean molecular weight of the absorbing organic matter in g/mol , ζ_i is the activity coefficient of compound i in the organic phase, and $p_{L,i}^\circ$ is the vapor pressure of the compound i in Torr. Using $T = 298 \text{ K}$, $MW_{om} = 412 \text{ g}/\text{mol}$ (assuming aerosol is mostly ozonide I, which is justified below), $\zeta_i = 1$ (an ideal solution), and $p_{L,I}^\circ = 4 \times 10^{-11} \text{ Torr}$ and $p_{L,II}^\circ = 4 \times 10^{-4} \text{ Torr}$ for ozonides I and II, we obtain $K_I = 1.1 \times 10^3$ and $K_{II} = 1.1 \times 10^{-4}$. The total yield of aerosol (total aerosol mass/reacted 1-tetradecene mass), Y , for this two-component mixture is

$$Y = Y_I + Y_{II} = (M_o\alpha_I K_I/1 + K_I M_o) + (M_o\alpha_{II} K_{II}/1 + K_{II} M_o) \sim \alpha_I + (M_o\alpha_{II} K_{II}/1 + K_{II} M_o) \quad (10)$$

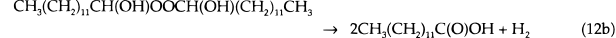
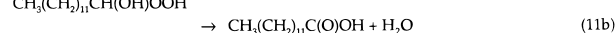
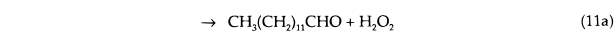
where Y_I and Y_{II} are the aerosol yields of ozonides I and II (aerosol ozonide mass/reacted 1-tetradecene mass) and α_I and α_{II} are the total (aerosol + gas) yields of ozonides I and II (total ozonide mass/reacted 1-tetradecene mass). The approximate form of the equation is valid in the following cases because $K_I M_o \gg 1$. We estimate α_I and α_{II} by assuming that the primary ozonide splits equally between reactions 1a and 1b (57), that all the large excited biradicals either decompose to form OH or are stabilized, and that no OH comes from small excited biradicals (4). The fraction of 1-tetradecene that forms large stabilized biradicals is then $0.50 - \text{OH yield} = 0.40$, for an OH yield of 0.10 (the value for 1-octene (58)). The fraction of small excited biradicals that are stabilized is 0.37 (4), so the fraction of 1-tetradecene that forms small stabilized biradicals is $0.5 \times 0.37 = 0.19$. Assuming that all stabilized biradicals react equally fast with tridecanal and formaldehyde, then half the large stabilized biradicals will form ozonide I and half will form ozonide II, and half the small stabilized biradicals will form ozonide II and half will form a volatile C2 ozonide. The total yields of ozonides I and II will therefore be $\alpha_I = 0.4/2 = 0.2$ and $\alpha_{II} = 0.4/2 + 0.19/2 = 0.3$, respectively. In two experiments using 0.5 and 1.5 ppmv of 1-tetradecene we measured particle mass concentrations of 1500 and 8000 $\mu\text{g}/\text{m}^3$. Using these values in eq 10 gives $Y_I = 0.20$, $Y_{II} = 0.04$, and $Y = 0.24$ for the first experiment and 0.20, 0.14, and 0.34 for the second. The calculated fraction of aerosol mass contributed by ozonides I and II are then 0.83 and 0.17 and 0.59 and 0.41, for experiments one and two, respectively. When a diffusion drier containing activated charcoal was placed in the SEMS sampling line to remove volatile components the aerosol mass decreased by $\sim 20\%$ in the second experiment, but no change was discernible in the first. Although they have considerable uncertainties, these results not only support the proposition that ozonide II is volatile enough to evaporate during TDPBMS sampling but also show that unless the total aerosol mass concentration in the chamber is very high, most of this compound will be present in the gas phase.

The presence of the 88 °C compound was apparent from shoulders on the 70 °C peak in the m/z 197 and 199 mass thermograms, but a mass spectrum could not be extracted because most features were too strongly masked by overlap with the other compound. The most likely identity of the 88

°C compound is α -hydroperoxytridecyl tridecanoate [$\text{CH}_3(\text{CH}_2)_{11}\text{CH}(\text{OC}(\text{O})(\text{CH}_2)_{11}\text{CH}_3)\text{OOH}$], which could form by reaction of tridecanoic acid with the large stabilized biradical (reaction 4). A standard of this compound prepared by liquid-phase ozonolysis desorbed at ~ 78 °C and had a large peak at m/z 197 due to the stable acylium ion, $\text{CH}_3(\text{CH}_2)_{11}\text{CO}^+$, which is characteristic of this class of compounds (23). In environmental chamber studies of ozonolysis of 1-decene in dry air (unpublished results), the details of which will not be discussed here, the corresponding compound, α -hydroperoxydecyl decanoate [$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{OC}(\text{O})(\text{CH}_2)_7\text{CH}_3)\text{OOH}$], is more easily identified in the aerosol.

The mass spectra of ozonides I and II and an ozonide III formed from gas-phase ozonolysis of 1-tetradecene in the presence of ~ 25 ppmv of pentanal (Figure 3D), have some similarities with the hydroperoxide and peroxide mass spectra in that intense peaks corresponding to the $\text{C}_n\text{H}_{2n-1}^+$ and $\text{C}_n\text{H}_{2n+1}^+$ series are observed up to m/z 125 as well as peaks at m/z 137, 138, 152, and 154. For the ozonides, the $\text{C}_n\text{H}_{2n-3}^+$ series is also intense with an especially prominent peak at m/z 123. Ozonides I and III have characteristic peaks at m/z 181 and M-17, M-33, and M-51, where M is the molecular ion mass ($M = 412$ and 300 for ozonides I and III), and the mass 17, 33, and 51 losses probably correspond to OH, HO_2 , and $\text{HO}_2 + \text{H}_2\text{O}$ or $\text{OH} + \text{H}_2\text{O}_2$. Ozonides II and III exhibit molecular ion peaks at m/z 244 and 300, respectively, and ozonide II has relatively strong peaks at m/z 180, 210, and 216. The only literature mass spectra for secondary ozonides formed from ozonolysis of normal alkenes is one for the small, symmetric C8 ozonide obtained from 4-octene (59). A small molecular ion peak was observed as well as some of the alkyl ion series seen here but not the m/z M-17, M-33, or M-51 peaks.

Gas Chromatographic Analysis of Aerosol Products Formed from Ozonolysis of 1-Tetradecene in Humid and Dry Air. Because GC-MS is widely used for determining organic aerosol composition, we have used it and GC-FID to analyze aerosol formed from ozonolysis of 1-tetradecene in humid and dry air for comparison with the results of TDPBMS analysis. GC-FID chromatograms of aerosol collected using a MOUDI impactor are shown in Figure 4. The major component in both cases is tridecanal, with tridecanoic acid being a minor component of the humid-air aerosol (Figure 4A) and relatively abundant in the dry-air aerosol (Figure 4B). A few other compounds are also present but could not be identified from their mass spectra. Except for tridecanoic acid, none of the mass spectra match those of aerosol compounds identified by TDPBMS. It is not likely that the discrepancy is due to evaporation of tridecanal and other compounds during TDPBMS sampling. Using eqs 9 and 10 and the assumption that 50% of the 1-tetradecene reacts by 1a to form tridecanal (57), which has a vapor pressure of $\sim 5 \times 10^{-3} \text{ Torr}$ (60), we estimate that tridecanal will only compose $\sim 4\%$ of the aerosol mass. A more likely explanation is that the compounds observed using GC-MS are decomposition products of the hydroperoxides, peroxides, and secondary ozonides identified by TDPBMS. The α -hydroxyalkyl hydroperoxides and bis(α -hydroxyalkyl) peroxides are known to thermally decompose primarily to aldehydes and carboxylic acids by loss of H_2O , H_2O_2 , or H_2 (61–64), which for HTHP and bis(α -hydroxytridecyl) peroxide should yield tridecanal and tridecanoic acid according to the reactions



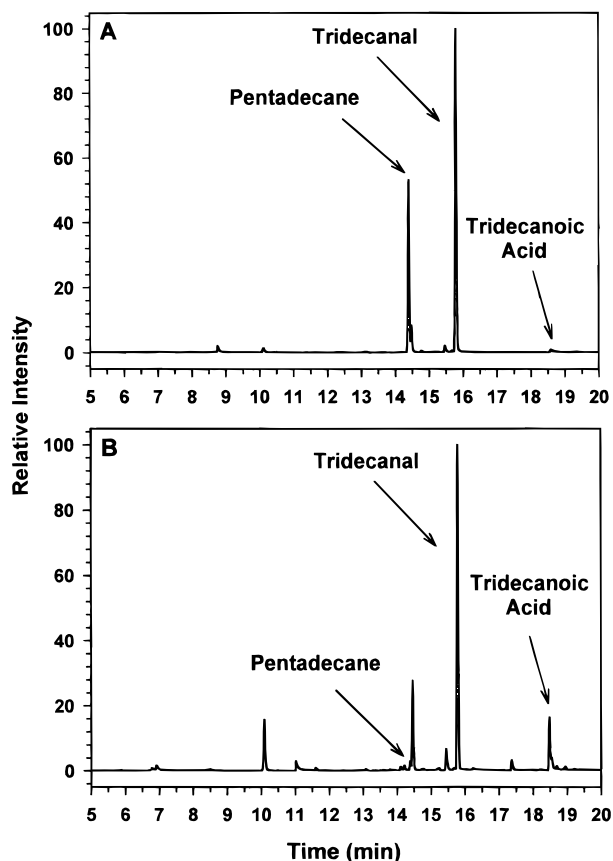
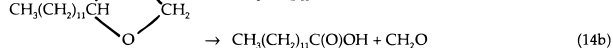
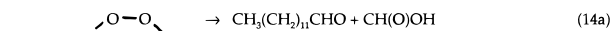
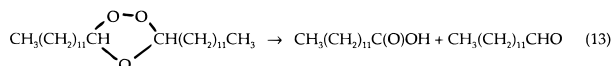
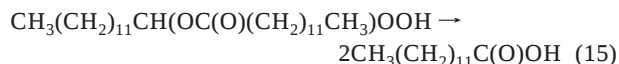


FIGURE 4. GC-FID chromatograms for aerosol formed from ozonolysis of 1-tetradecene in (A) air with 30% relative humidity and (B) dry air. Compounds were identified by comparison with retention times of authentic standards and by GC-MS performed under the same conditions. Pentadecane was used as an internal standard.

Secondary ozonides also thermally decompose primarily to aldehydes and carboxylic acids (65–67), which for ozonides I and II should yield tridecanal, tridecanoic acid, formic acid, and formaldehyde according to the reactions



Although we have not carried out GC-MS analysis of α -hydroperoxytridecyl tridecanoate, the acids are regenerated during thermal decomposition of such compounds (43), which in this case would lead to tridecanoic acid by the reaction



The narrow chromatographic peaks and similar retention times of tridecanal and tridecanoic acid in samples and standards indicates that decomposition occurs before the compounds travel very far along the column. Because of their low vapor pressures, chromatography of parent compounds would require temperatures well above 200 °C (tridecanal, with a 25 °C vapor pressure of $\sim 5 \times 10^{-3}$ Torr, appears at ~ 210 °C), which is sufficiently high for rapid decomposition (61, 67). In experiments not described here, the products obtained from ozonolysis of 7-tetradecene

$[\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3]$, which are more volatile than those from 1-tetradecene, yielded broad chromatographic peaks that are indicative of decomposition on the column. The proportions of tridecanal/tridecanoic acid/unknowns determined from GC-FID analyses of 1-tetradecene ozonolysis products were approximately 0.84/0.04/0.12 for the humid-air reaction and 0.56/0.13/0.31 for the dry-air reaction. The high proportions of tridecanal indicate that HTHP and bis(α -hydroxytridecyl) peroxide decompose primarily by loss of H_2O_2 via reactions 11a and 12a and that ozonide II decomposes primarily by reaction 14a. Unfortunately, our GC method would not allow for analysis of formaldehyde and formic acid, tridecanoic acid does not GC very well, and we could not identify other products, so a more complete understanding of the thermal decomposition process could not be obtained. It is worth noting that samples also decompose and polymerize as they age, by reactions that are catalyzed by acids (24), leading to different product distributions from GC-FID analysis. For example, after 1 week the proportions of tridecanal and tridecanoic acid in the dry-air aerosol had reversed to 0.16 and 0.66, respectively.

These results help to explain our previous analyses of tridecanoic acid in dry-air aerosol, in which the concentration measured by GC-FID was $\sim 35\%$ higher than the TDPBMS value (21). In that study the TDPBMS was calibrated using tridecanoic acid, and the aerosol concentration was quantified using the molecular ion peak at m/z 214. We now know that ozonide I contributes to this peak and upon decomposition also contributes to tridecanoic acid measured by GC-FID (as opposed to the asymmetric ozonide II, which should decompose primarily by reaction 14a (65) and therefore contribute little to the tridecanoic acid measured by GC-FID). A combination of these factors probably accounts for the discrepancy in TDPBMS and GC-FID measurements.

These experiments may also explain the results of a recent chamber study that employed GC-MS to determine the composition of filter-collected aerosol formed by ozonolysis (with some contribution from OH reactions) of 1-octene and 1-decene in humid air (13). The major products from 1-octene were heptanal, heptanoic acid, and dihydro-5-propyl-2(3H)-furanone, and from 1-decene they were nonanal, nonanoic acid, and dihydro-5-pentyl-2(3H)-furanone. Gas-particle partitioning calculations indicate that these compounds are too volatile (i.e. nonanoic acid has the lowest vapor pressure at $\sim 2 \times 10^{-3}$ Torr ~ 2 ppmv (60)) to form much aerosol at the 2–8 ppmv alkene concentrations used in the experiments. Instead, these compounds were probably decomposition products of α -hydroxyalkyl hydroperoxides, dihydroxyalkyl peroxides, α -acyloxyalkyl hydroperoxides, and, possibly, secondary ozonides.

Implications for Atmospheric Aerosol Chemistry

Although the amount of atmospheric aerosol formed from normal alkenes appears to be relatively small (17), these compounds provide a good starting point for understanding the chemical mechanisms by which alkenes in general participate in atmospheric aerosol nucleation and growth through reactions with O_3 . The gas-phase and liquid-phase O_3 chemistry of normal alkenes is simpler and has been more thoroughly studied than that of the cyclic alkenes (especially those of biogenic origin), and liquid-phase ozonolysis of normal alkenes provides a simple and efficient means for generating a number of standard hydroperoxide and secondary ozonide compounds that have been critical for our mass spectral identification of environmental chamber aerosol products. In our work we have used 1-tetradecene as a surrogate for this class of compounds because its relatively high molecular weight and terminal double-bond enhance aerosol formation. Smaller normal alkenes or those with internal double bonds will generally form less aerosol

TABLE 1. Calculated 25 °C Vapor Pressures and Gas-Particle Partition Coefficients of Potential Products of 1-Tetradecene Ozonolysis in Humid and Dry Air

compound	vapor pressure ^a $p_{L,i}$ (Torr)	partition coeff ^b K_i (m ³ /μg)	$C_{p,i}/(C_{p,i} + C_{g,i})^c$	
			1000	10
formaldehyde	4×10^3	2×10^{-11}	0	0
formic acid	30	2×10^{-9}	0	0
1-tetradecene	3×10^{-2}	2×10^{-6}	0	0
tridecanal	5×10^{-3}	1×10^{-5}	0.01	0
C14 ozonide II	4×10^{-4}	2×10^{-4}	0.17	0
tridecanoic acid	7×10^{-6}	9×10^{-3}	0.90	0.08
α-hydroperoxytridecyl formate	8×10^{-9}	8	1.00	0.99
α-hydroxytridecyl hydroperoxide	3×10^{-9}	20	1.00	1.00
α-hydroxytridecyl-α'-hydroxymethyl peroxide	4×10^{-10}	2×10^2	1.00	1.00
α-hydroperoxytridecyl tridecanoate	4×10^{-11}	2×10^3	1.00	1.00
C26 ozonide I	4×10^{-11}	2×10^3	1.00	1.00
bis(α-hydroxytridecyl) peroxide	3×10^{-11}	2×10^3	1.00	1.00
α-formyloxy-α'-hydroxyditridecyl peroxide	2×10^{-13}	3×10^5	1.00	1.00

^a Calculated from TPTD desorption temperatures using a correlation and data described previously (23) along with data from this study.

^b Calculated using eq 9, the values of $p_{L,i}$ from this table, and assuming $MW_{om} = 300$ g/mol and $\zeta_i = 1$. ^c Calculated using eq 9 in the form $C_{p,i}/(C_{p,i} + C_{g,i}) = (1 + 1/K_i M_o)^{-1}$, the partition coefficients, K , and particulate organic mass concentrations, M_o , of 1000 and 10 μg/m³.

because of the lower molecular weights of the products (e.g. 7-tetradecene will initially form C7 biradicals, heptanal, and heptanoic acid).

The results reported here and in our related study (23) demonstrate that the aerosol products formed from ozonolysis of 1-tetradecene in air can be explained in terms of the Criegee mechanism, which is well established from numerous liquid-phase studies (24). Depending on the relative concentrations of aldehydes and acidic species such as water, alcohols, and carboxylic acids, the products may include secondary ozonides, α-hydroxy, α-alkoxy, and α-acyloxy tridecyl hydroperoxides, and peroxyhemiacetals, in addition to tridecanoic acid. With the exception of the peroxyhemiacetals, which are apparently formed by a heterogeneous reaction mechanism, the products are similar to those observed from gas-phase ozonolysis of the smallest alkene, ethene (29–32).

Aerosol products of normal alkene ozonolysis can be formed from rearrangement of an excited Criegee biradical to form a carboxylic acid and from reactions of stabilized biradicals. In the ambient atmosphere, water, alcohols, carboxylic acids, and aldehydes compete with each other in stabilized biradical reactions. The relative rates of reaction of formic acid, formaldehyde, and water with CHOO have been measured and are ~14000:700:1, and the rate with methanol is significantly slower than with formic acid but faster than with water (31). However, although water reacts much more slowly than competing organic compounds, because of the higher atmospheric concentrations of water vapor compared to these species (~10⁷ ppb: 1–10 ppb (68, 69)) the major reaction products are expected be α-hydroxy-alkyl hydroperoxides. These compounds can subsequently react with aldehydes, which in ambient air consist primarily of formaldehyde and acetaldehyde (68, 69), to form peroxyhemiacetals. Whether or not any of these compounds form aerosol, either through nucleation or condensation, depends primarily on their vapor pressures. For example, the 25 °C vapor pressures of many of the potential aerosol and gas-phase products of 1-tetradecene ozonolysis in humid and dry air are shown in Table 1. These values were calculated from TPTD desorption temperatures using a correlation and data described elsewhere (23), along with data from this study. Based on uncertainties in desorption temperatures and scatter in the correlation, the values are probably accurate to within about an order of magnitude. The gas-particle partition coefficients in the table were calculated using eq 9, the vapor pressures, and the assumption that $MW_{om} = 300$ g/mol and $\zeta_i = 1$. The fractions of each compound in particles,

$C_{p,i}/(C_{p,i} + C_{g,i})$, which are also given in Table 1, were calculated using eq 9 [in the form $C_{p,i}/(C_{p,i} + C_{g,i}) = (1 + 1/K_i M_o)^{-1}$], the partition coefficients, and particulate organic mass concentrations of 1000 and 10 μg/m³, which are representative of our chamber experiments and the polluted atmosphere (5, 6), respectively. With the exception of tridecanoic acid, all the compounds that form aerosol in the chamber or would partition into ambient aerosol are formed by reactions of aldehydes, water, or carboxylic acids with stabilized biradicals and subsequent hydroperoxide-aldehyde reactions. The vapor pressures of the hydroperoxides, peroxyhemiacetals, and secondary ozonide I are lower than that of tridecanoic acid by factors of ~10³–10⁷. As was mentioned above, evaporation during TDPBMS sampling of compounds with vapor pressures greater than ~10⁻⁵ Torr is not a serious problem since in the ambient atmosphere they would be predominantly in the gas phase. Looked at in another way, this process “prevents” us from observing compounds in chamber aerosols that would not be there if we were performing experiments at atmospheric aerosol concentrations.

Formation of even trace levels of low-volatility hydroperoxides or secondary ozonides from reactions of relatively large stabilized biradicals and carboxylic acids, aldehydes, and perhaps water, could play a role in atmospheric nucleation (23, 70).

However, in most cases, compounds with sufficiently low vapor pressures will partition into preexisting aerosol, primarily in the fine particle mode (5). Particles of this size are efficiently respired and therefore provide a route by which organic hydroperoxides and the corresponding peroxyhemiacetals can be transported and deposited onto deep-lung surfaces. Because of their oxidizing properties and presence in fine particles, hydroperoxides and peroxides are considered to be one of the possible causative agents for the adverse effects of PM-2.5 on human health (33). The observation that the compounds generated in our environmental chamber reactions are stable for at least hours in the chamber and days in solution indicates that the lifetimes are long enough for transport and deposition to occur. However, their fate in the atmosphere is unknown. Hydroperoxides can photolyze in the troposphere (71), and although thermal decomposition rates at ambient temperatures (66, 67) are negligible compared to rates of other removal processes, decomposition can be catalyzed by acids (50).

The organic hydroperoxides, peroxides, and secondary ozonides that made up nearly all the aerosol mass in our experiments decompose to aldehydes and carboxylic acids

during GC analysis. Similar behavior could occur with other types of labile compounds formed in photochemical reactions. Investigators using GC-MS in future studies of organic aerosol chemistry should therefore be aware of the potential for sample alteration, such as compound decomposition or polymerization, due to aging, chemical processing, or thermal effects. The TDPBMS technique avoids many of these problems and also provides a relatively simple means for estimating compound vapor pressures, which is an extremely valuable quantity for modeling gas-particle partitioning. But in TPTD analysis it can be difficult to resolve compounds with similar vapor pressures, and sampling losses may occur for compounds that have vapor pressures greater than $\sim 10^{-5}$ Torr (although our earlier discussion indicates that the latter is probably not a significant problem for chamber studies). It may be possible to overcome some of the difficulties associated with off-line analysis by using derivatization techniques, lower GC temperatures, or HPLC. Because aerosol compound standards are usually not commercially available, it would be quite valuable if the GC-MS derivatization technique developed by Yu, Flagan, and Seinfeld (14) for compound identification could be used in aerosol studies without concern for artifacts.

At this time it is therefore preferable to use a combination of techniques for aerosol analysis. We are currently taking this approach for studies of reactions of O_3 with other alkenes, including cyclic compounds of anthropogenic and biogenic origin, to compare the aerosol chemistry of these compounds with that of normal alkenes. We are also investigating the rates at which alcohols, carboxylic acids, and aldehydes of various types as well as water, SO_2 , NO , and NO_2 react with Criegee biradicals. Such studies are necessary for developing quantitative models and also for applying the results of environmental chamber reactions to the ambient atmosphere, where VOC concentrations are often 2–3 orders of magnitude lower. As was seen here for normal alkene ozonolysis, when first-generation reaction products reach high enough concentrations to participate in secondary reactions, initial VOC concentrations can have a dramatic effect on the chemical mechanisms of aerosol formation. The results of these studies should provide further insight into secondary organic aerosol chemistry and be useful to atmospheric modelers and those interested in the potential health effects of hydroperoxides and peroxides.

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