Formation of Alkoxyhydroperoxy Aldehydes and Cyclic Peroxyhemiacetals from Reactions of Cyclic Alkenes with O_3 in the Presence of Alcohols

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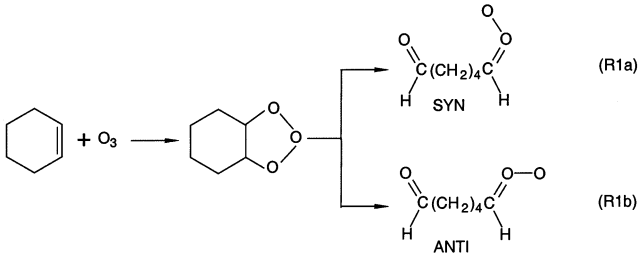
Received: September 20, 2002; In Final Form: January 24, 2003

A thermal desorption particle beam mass spectrometer has been used to investigate the products and mechanisms of secondary organic aerosol formation from reactions of O_3 with cyclohexene, cycloheptene, cyclooctene, and cyclodecene in the presence of alcohols. Alkoxyhydroperoxy aldehydes formed through reactions of stabilized Criegee intermediates with alcohols have been identified by comparison of aerosol mass spectra with those of standards synthesized in solution. These compounds can subsequently isomerize through an intramolecular reaction between the hydroperoxyl and carbonyl groups to form a cyclic peroxyhemiacetal. For example, in the reaction of O_3 with cyclodecene in the presence of 1-propanol the product of the reaction of the stabilized Criegee intermediate with 1-propanol is 10-*n*-propoxy-10-hydroperoxydecanal, which can then cyclize to 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane. Experiments performed by monitoring reactions of alkoxyhydroperoxy aldehyde standards added to the environmental chamber indicate that the cyclization reaction occurs in the gas phase, but apparently not in the particle phase, and occurs under thermal conditions. The alkoxyhydroperoxy aldehydes appear to undergo little, if any, intermolecular reaction to form dimers or polymeric peroxyhemiacetals.

Introduction

Atmospheric reactions of O_3 with biogenic alkenes, such as the cyclic monoterpenes [$C_{10}H_{16}$] α-pinene and *β*-pinene, are potentially an important source of global secondary organic aerosol (SOA).[1] The reactions have been the subject of a number of studies that have sought to identify and quantify both gas-phase and particle-phase products and to develop mechanisms by which they are formed.[2−4] It is generally assumed that SOA formation occurs by condensation of low-volatility products of gas-phase oxidation reactions,[5] but recent studies have indicated that heterogeneous reactions,[6] sometimes catalyzed by acids,[7] may also be important. It has been shown that SOA products of alkene−O_3 reactions are comprised of multifunctional compounds containing various combinations of carbonyl, hydroxyl, and carboxyl groups, but the proposed reaction mechanisms are complicated and are still rather speculative. Studies on simple alkenes can help in unraveling the mechanisms by which more complex molecules react, and have, in conjunction with solution-phase studies,[8] provided much of the basis for what is currently known about gas-phase alkene−O_3 chemistry.[9,10]

Reactions of O_3 with alkenes are initiated by addition of O_3 to the double bond to form an energy-rich primary ozonide, which decomposes. For compounds with endocyclic double bonds, such as cyclohexene [C_6H_{10}], the decomposition product is an excited bifunctional Criegee intermediate containing both carbonyl and carbonyl oxide moieties, [$OHC(CH_2)_4CHOO$]*, which is formed in both syn (R1a) and anti (R1b) conformations.[11]



For acyclic compounds or compounds with exocyclic double bonds, the primary ozonide splits into two pairs of molecules with one molecule in each pair containing the carbonyl moiety and the other (i.e., the excited Criegee intermediate) containing the carbonyl oxide moiety. For example, for the terminal alkene 1-tetradecene [$CH_3(CH_2)_{11}CH{=}CH_2$] the products are [$CH_3(CH_2)_{11}CHOO$]* (syn and anti isomers) + HCHO (R3a,b) and [CH_2OO]* + $CH_3(CH_2)_{11}CHO$ (R3c).

Excited Criegee intermediates can subsequently isomerize, decompose, or undergo collisions with third bodies (N_2, O_2 for reaction in air) to form stabilized Criegee intermediates (SCI). Recent evidence indicates that the sole reaction pathway for syn isomers (excited and stabilized) is unimolecular decomposition through the so-called "hydroperoxide channel" to form OH radicals and radical coproducts.[12,13] Anti isomers can isomerize and decompose, with some channels leading to OH radicals.[14] After stabilization, they also can undergo association reactions with acidic species, such as water, carboxylic acids, and alcohols to form hydroperoxides (not to be confused with the hydroperoxide channel), with aldehydes and ketones to form secondary ozonides, and O-atom abstraction reactions with SO_2, NO_2, and CO to form an aldehyde or ketone.[9,10,15]

It is thought that for reactions of O_3 with cyclic monoterpenes, such as α-pinene and *β*-pinene, the major pathways to SOA

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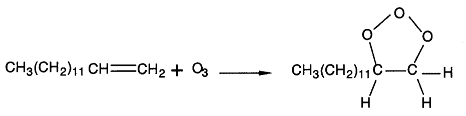
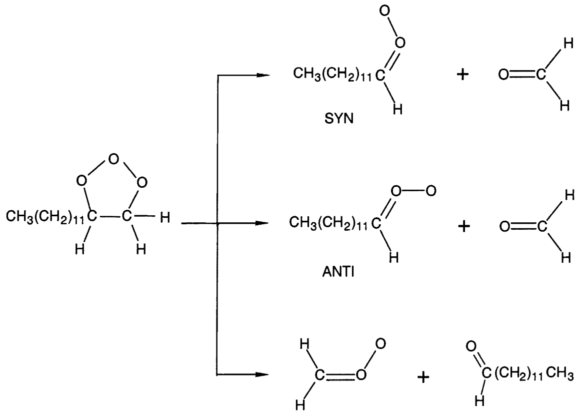


(R2)

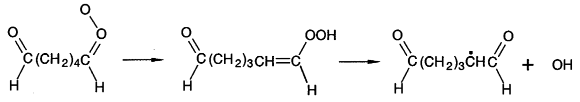


(R3a)

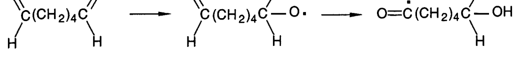
(R3b)

(R3c)

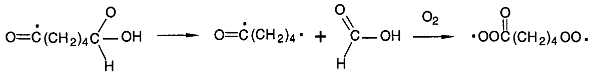
products are through the hydroperoxide channel.[2,3] This channel can, for example, lead to acyl peroxy radicals, which are key intermediates in the formation of low-volatility dicarboxylic acids.[16,17] The SOA pathways may be slightly different for simple cyclic alkenes, such as cyclohexene and homologous compounds. Like α-pinene, they have an endocyclic double bond (β-pinene has an exocyclic double bond), but because they lack a vinylic methyl substituent, some of the reaction pathways that can occur for α-pinene are not possible. In a recent study of the reaction of O_3 with cyclohexene,[18] I proposed a mechanism for the formation of dicarboxylic acids and other aerosol compounds in which acyl peroxy radicals were not formed through the hydroperoxide channel (R4), which involves abstraction of an allylic hydrogen, but through channels involving abstraction of an aldehydic hydrogen from the anti isomer, as in (R5), for example, followed by decompostion and reaction with O_2 (R6). These reactions have also been proposed to lead to the formation of 5-oxoperoxypentanoic acid, which has been identified recently among the gas-phase products of the reaction of cyclohexene and O_3 using atmospheric pressure ionization mass spectrometry.[19]



(R4)

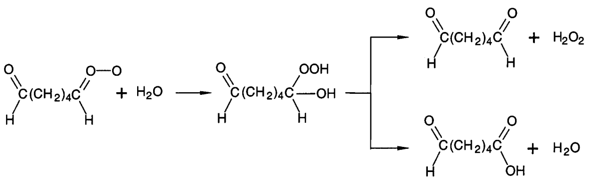


(R5)



(R6)

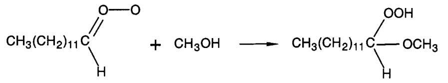
In the atmosphere, SCI from cyclic alkenes are expected to react primarily with water to form hydroxyhydroperoxides.[15,20] These reactions probably do not contribute significantly to SOA formation, however, because although hydroxyhydroperoxides from acyclic alkenes have been observed,[21−23] those formed from cyclic alkenes (with the exception of camphene[24]) appear to decompose by loss of H_2O_2 and H_2O to rather volatile aldehydes and carboxylic acids, respectively.[4,17,19,24] The reactions for cyclohexene are



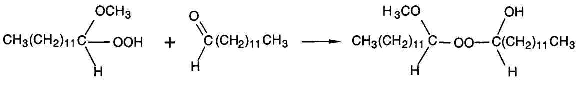
(R7a)

(R7b)

In my previous study on cyclohexene,[18] reactions of SCI with scavengers other than water, including methanol, 2-propanol, and formaldehyde, also did not lead to aerosol formation. These results were quite different from what we observed earlier for reactions of O_3 with acyclic alkenes. In studies of the ozonolysis of 1-tetradecene,[6,22] we found that nearly all the aerosol was formed through reactions of SCI scavengers with $CH_3(CH_2)_{11}$-CHOO, the SCI formed in R3b. For example, for reaction in the presence of methanol the major aerosol products were α-methoxytridecyl hydroperoxide [$CH_3(CH_2)_{11}CH(OCH_3)OOH$] (R8) and α-methoxy-α'-hydroxytridecyl peroxide [$CH_3(CH_2)_{11}$-$CH(OCH_3)OOCH(OH)(CH_2)_{11}CH_3$] (R9), a peroxyhemiacetal formed by reaction of α-methoxytridecyl hydroperoxide with tridecanal formed from (R3c).



(R8)



(R9)

The dramatic differences observed in the composition of SOA formed from cyclic and acyclic alkenes led me to wonder to what extent and under what conditions reactions of SCI with scavengers might be involved in SOA formation from ozonolysis of cyclic alkenes. Here I report on an investigation of SOA formation from reactions of O_3 with cyclohexene, cycloheptene, cyclooctene, and cyclodecene in the presence of alcohols, in which a thermal desorption particle beam mass spectrometer (TDPBMS) was used for SOA analysis. Alcohols are good probes for evaluating the formation of SOA through SCI reactions because standards of the alkoxyhydroperoxide products of the reactions can be synthesized in solution and have characteristic TDPBMS mass spectra, which can be used for compound identification. The study aids the development of a more cohesive understanding of the similarities and differences in the reactions of O_3 with simple cyclic and acyclic alkenes, and provides an important stepping stone for studies of the more complex monoterpenes currently underway in our laboratory.

Experimental Section

Materials. Cyclohexene (99%), cycloheptene (97%), cyclooctene (95%), 1-octene (98%), adipic acid (99%), pimelic acid (98%), azelaic acid (98%), and sebacic acid (99%) were obtained from Aldrich Chemical, Inc., and cyclodecene (95%) was obtained from Chemsampco, Inc. HPLC grade methanol, 1-propanol, acetonitrile, and water were obtained from Fisher Scientific. Chemicals were used without purification.

Aerosol Mass Spectrometric Analysis by TDPBMS and TPTD. Detailed descriptions of the TDPBMS and its operation for real-time analysis[25] and temperature-programmed thermal desorption (TPTD)[26] are presented elsewhere. Aerosol is sampled into the TDPBMS through a 100 μm orifice, which maintains the flow at 0.075 L min^{-1} and reduces the pressure from atmospheric to 300 Pa. Particles then enter a tube containing a series of aerodynamic lenses,[27,28] which focus the particles into a narrow, low-divergence beam for transport through two flat-plate skimmers separating three differentially pumped chambers. In the detection chamber (~10^{-5} Pa), particles with diameters of ~0.02−0.5 μm impact with ~40−100% efficiency on the walls of a V-shaped notch (0.4 cm × 0.4 cm opening, 0.7 cm deep) in the end of a 0.635 cm diameter copper rod positioned at the entrance to the ionizer of a quadrupole mass spectrometer. The rod is resistively heated by tungsten wire threaded through a series of five holes located 1 to 2.5 cm behind the notch. Each hole contains a cylindrical alumina insert to electrically insulate the tungsten wire from the copper rod. The vaporizer temperature is monitored by a thermocouple inserted 0.5 cm behind the notch and is regulated by a temperature controller using Labview software. The vaporizer is either heated continuously at 165 °C for real-time TDPBMS analysis or cooled by an external liquid nitrogen bath for collection of particles for TPTD. After vaporization, molecules diffuse into an ionizer where they are impacted by 70 eV electrons and the ions are mass analyzed in a quadrupole mass spectrometer equipped with a conversion dynode/pulse counting detector.

Particle analysis by TPTD was carried out on ~1 μg of aerosol collected in ~15 min on the vaporizer at −30 °C. The sample was first allowed to warm to −5 °C by removing the liquid nitrogen bath, and was then desorbed under controlled conditions by heating at a linear ramp rate of 2 °C min^{-1} up to ~125 °C while mass spectra were continuously recorded. During TPTD, aerosol components desorb according to volatility so mass spectra of individual compounds can be extracted from the time-dependent mass spectra. The desorption profile also provides information on compound vapor pressures.[22,26,29]

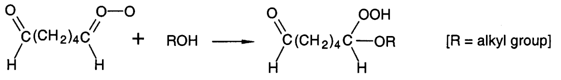
Because particles are exposed to subsaturated air inside the TDPBMS, sufficiently volatile compounds could evaporate prior to analysis. Calculations and experiments with compounds of known vapor pressures indicate that particulate compounds having vapor pressures less than ~10^{-2} Pa undergo negligible evaporation in transit to the vaporizer. When particles are collected on the vaporizer for TPTD analysis, they are cooled in less than a microsecond to −30 °C, reducing the vapor pressure to such a low value that essentially no evaporation occurs until the vaporizer is heated. Evaporation does not pose a problem for the present study because the focus is on compounds with vapor pressures less than ~10^{-2} Pa. Compounds with higher vapor pressures are expected to be primarily in the gas phase prior to entering the TDPBMS.

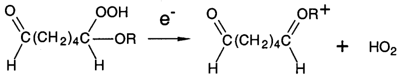
Generation of Aerosol Standards for TDPBMS Analysis. As an aid in identifying aerosol components formed in environmental chamber reactions, alkoxyhydroperoxy aldehyde standards were synthesized and analyzed by TDPBMS using the same method as in our previous studies of 1-tetradecene.[6] Liquid-phase ozonolyses of cyclohexene, cycloheptene, cyclooctene, and cyclodecene in an alcohol solvent were carried out on ~6−10 mM solutions prepared by dissolving 10 μL of alkene in either 10 mL of methanol or 1-propanol. Ozone from a Welsbach T-408 O_3 generator (~2% O_3/O_2) was then bubbled through the solutions at 1.5 L min^{-1} for ~5 s, which was sufficiently long to ozonize nearly all the alkene without adding excess O_3. For terminal alkenes, this method has been shown to produce alkoxyalkyl hydroperoxides in nearly quantitative yields.[30] For cyclohexene and cycloheptene, reacted solutions were atomized in a Collison atomizer using dry, clean air (RH ~ 0.1% and hydrocarbons <5 ppbv) from an Aadco pure air generator as the carrier gas. Aerosol from the atomizer was passed through diffusion dryers containing activated charcoal to adsorb the alcohol, unreacted alkene, and volatile reaction products, which evaporate from the particles. The residual, low-volatility particles were then sampled into the TDPBMS for TPTD analysis. For cyclooctene and cyclodecene, solution products were first separated using an Agilent 1100 Series high-performance liquid chromatograph (HPLC). The HPLC contained a 150 mm × 4.6 mm Eclipse 5 μm XDB-C8 reversed-phase column that was operated at room temperature, and the mobile phase was an isocratic mixture of 65% acetonitrile:35% water flowing at 1.5 mL min^{-1}. A microsyringe was used to inject 20 μL of solution onto a sampling loop. Downstream of the column, separated components were converted to an aerosol by inserting the fused silica-coated capillary tube carrying the column effluent into one of the sampling channels of the Collison atomizer. The aerosol then passed through the diffusion dryers and into the TDPBMS for real-time analysis. Solutions of adipic acid, pimelic acid, azelaic acid, and sebacic acid in 1-propanol were atomized and analyzed by real-time TDPBMS.

Environmental Chamber Technique. Secondary organic aerosol was formed in a series of environmental chamber experiments from reactions of O_3 with cyclohexene, cycloheptene, cyclooctene, and cyclodecene in the presence of alcohols. Aerosol was formed by reacting ~1−2 ppmv of the cyclic alkene with ~2.6 ppmv of O_3 in an ~7000 L PTFE film chamber at room temperature (~23 °C). The chamber was filled with dry, clean air (RH ~ 0.1% and hydrocarbons <5 ppbv). Approximately 2000 ppmv of 1-propanol or 4000 ppmv of methanol was added to the chamber to react with stabilized Criegee intermediates and to scavenge >98% of the OH radicals formed in the alkene-O_3 reaction,[31] thereby eliminating products from OH reactions with the alkene. In one cyclodecene experiment, the air was humidified to ~30% RH and ~1000 ppmv of cyclohexane was added to the chamber to scavenge OH radicals, whereas in another cyclodecene experiment, ~100 ppmv of formaldehyde and ~1000 ppmv of cyclohexane were added. The alkenes, alcohols, paraformaldehyde, and water were added to the chamber by evaporating the heated liquids or solids from a glass bulb into a clean air stream. Ozone was added to the chamber last by flowing clean air through a 0.5 L bulb containing ~2% O_3/O_2. During all chemical additions, a fan was run to mix the chamber contents and was then turned off. Aerosol formed by homogeneous nucleation, usually within a minute of adding O_3, and was sampled directly into the TDPBMS through stainless steel tubing (0.635 cm o.d. and 30 cm long up to the TDPBMS sampling orifice) inserted into a port in the chamber wall. Particles were either analyzed in real-time or by TPTD. In some experiments, aerosol size distributions were measured using a scanning mobility particle sizer (SMPS).[25,32] Particle concentrations were initially less than ~10 cm^{-3} and then reached ~10^4−10^5 cm^{-3} a few minutes after adding O_3. Average particle diameters were ~0.2−0.4 μm. Aerosol wall losses are ~15% h^{-1} for these experiments.[20] Ozone concentrations were measured by drawing air through PTFE tubing into a Dasibi 1003-AH O_3 analyzer. After an experiment the chamber was evacuated, filled, and flushed until the next day or longer (>10 chamber volumes).

Results and Discussion

SOA Formation from Reactions of O_3 with Cyclohexene and 1-Octene in the Presence of Alcohols. In my previous study of the reactions of cyclohexene with O_3,[18] the addition of methanol [CH_3OH], 2-propanol [$CH_3CH(OH)CH_3$], formaldehyde [HCHO], or water to the environmental chamber did not significantly affect particle mass spectra [especially the *m*/*z* 99 and 115 peaks (*m*/*z* = mass/charge) used in the identification of low-volatility species involved in nucleation], leading me to conclude that reactions of SCI with scavengers were not important in SOA formation. The mass spectra obtained for the reactions in the presence of methanol and 2-propanol are shown in Figures 1A and 1B, respectively. The peaks I expected to see change if alkoxyhydroperoxy aldehydes were present were based on our earlier observations for 1-tetradecene,[6] which showed that the highest mass in an alkoxyalkyl hydroperoxide mass spectrum was $m/z = [\mathrm{M}-33]^+$ (M = mass of parent molecule) due to HO_2 loss from the molecular ion. In the cyclohexene reaction in the presence of an alcohol [ROH], alkoxyhydroperoxy aldehyde products would be formed through SCI reactions (R10) that are similar to (R8). During mass analysis, the compound would be ionized and lose HO_2 (R11).


$$\mathrm{HC(O)(CH_2)_4CH(O{-}O)} + \mathrm{ROH} \longrightarrow \mathrm{HC(O)(CH_2)_4CH(OOH){-}OR} \quad [\mathrm{R = alkyl\ group}]$$
(R10)


$$\mathrm{HC(O)(CH_2)_4CH(OOH){-}OR} \xrightarrow{e^-} \mathrm{HC(O)(CH_2)_4CH{=}OR^+} + \mathrm{HO_2}$$
(R11)

In the methanol and 2-propanol reactions, mass peaks would therefore be expected at *m*/*z* 129 and 157 due to the $OHC(CH_2)_4CHOCH_3^+$ and $OHC(CH_2)_4CHOCH_2(CH_3)_2^+$ ions, respectively. Although a small peak is present at *m*/*z* 129 in the methanol reaction (Figure 1A), the peak does not decrease when the alcohol is changed to 2-propanol (Figure 1B), nor does a detectable peak appear at *m*/*z* 157.

For purposes of comparison, aerosol mass spectra obtained from reaction of the acyclic alkene 1-octene [$CH_3(CH_2)_5CH{=}CH_2$] in the presence of methanol and 2-propanol are shown in Figures 1C and 1D, respectively. The alkoxyalkyl hydroperoxides $CH_3(CH_2)_5CH(OCH_3)OOH$ and $CH_3(CH_2)_5CH(OCH_2(CH_3)_2)OOH$ expected to be formed as in (R2, R3b, and R8), should lose HO_2 as in (R11) when ionized, forming $CH_3(CH_2)_5CHOCH_3^+$ and $CH_3(CH_2)_5CHOCH_2(CH_3)_2^+$ ions that yield peaks at *m*/*z* 129 and 157, respectively. In changing from methanol to 2-propanol the only significant change in the mass spectra is the disappearance of *m*/*z* 129 and appearance of *m*/*z* 157, indicating that the alkoxyalkyl hydroperoxides are present in the aerosol.

One explanation for the difference between the aerosol products formed in the reactions of cyclohexene and 1-octene in the presence of alcohols is that the alkoxyhydroperoxy aldehydes formed from cyclic alkenes are not stable. This appears to be the case for reactions with water, even though stable hydroxyalkyl hydroperoxides have been observed from reactions of acyclic alkenes.[21−23] It could also be that, although alkoxyhydroperoxides are formed in both reactions, the cyclohexene products are more volatile and so do not form significant aerosol under these conditions. Because the compounds have similar structures and molecular weights, however, this is not a likely explanation. Another possibility is that the concentrations of alkoxyhydroperoxides were much lower in the cyclohexene reactions, so less aerosol was formed. Although the concentrations of cyclohexene and 1-octene were similar in these experiments, the SCI yields are 3% for cyclohexene[33] compared to 35% for 1-octene.[24]

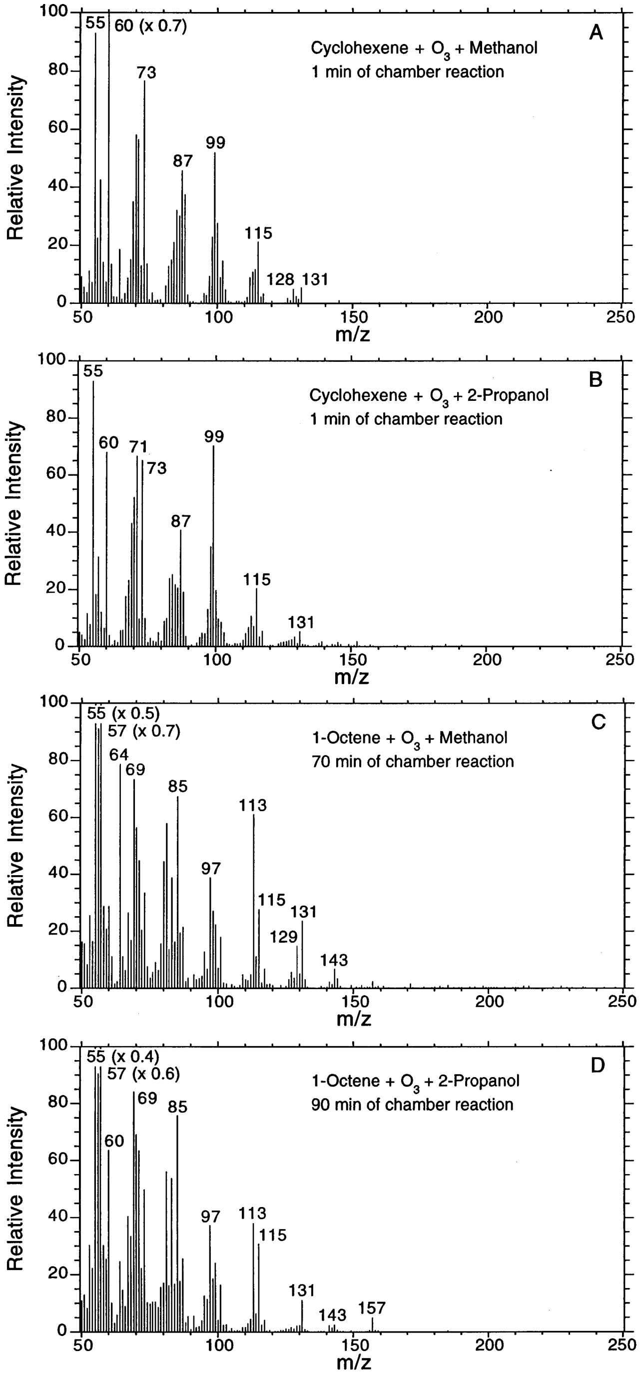


Figure 1. Real-time TDPBMS mass spectra of aerosol formed in the environmental chamber reaction of O_3 with (A) cyclohexene in the presence of methanol after 1 min, (B) cyclohexene in the presence of 2-propanol after 1 min, (C) 1-octene in the presence of methanol after 70 min, and (D) 1-octene in the presence of 2-propanol after 90 min. The alcohol acts as an OH radical scavenger and a stabilized Criegee intermediate (SCI) scavenger.

SOA Formation from Reactions of O_3 with Cyclohexene, Cycloheptene, and Cyclooctene in the Presence of Alcohols. One interesting observation in my cyclohexene study,[18] which was not relevant to the issue of nucleation, was that when the reaction was run with 2-propanol (it was mistakenly reported that 1-propanol was used) the peak at *m*/*z* 113 grew in a little more strongly later in the reaction than it did with or without the methanol, water, or formaldehyde SCI scavengers. More recent experiments showed that when 1-propanol [$CH_3CH_2CH_2OH$] was used the *m*/*z* 113 peak grew in even more rapidly, and that later in the experiment a small peak was detectable at

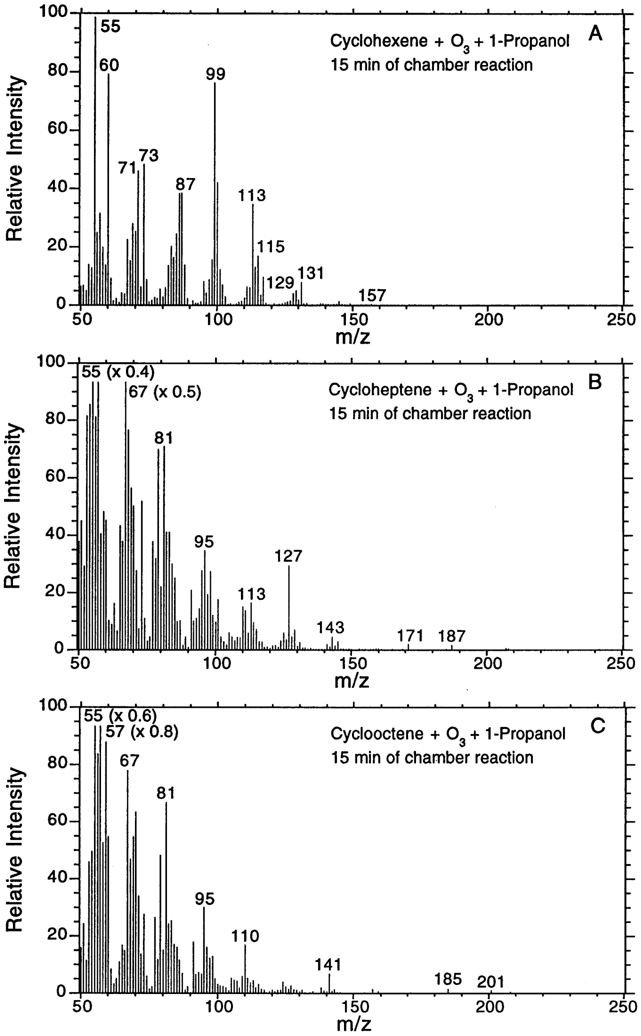


Figure 2. Real-time TDPBMS mass spectra of aerosol formed in the environmental chamber after 15 min of reaction of O_3 with (A) cyclohexene, (B) cycloheptene, and (C) cyclooctene in the presence of 1-propanol. The 1-propanol acts as an OH radical scavenger and a stabilized Criegee intermediate (SCI) scavenger.

m/z 157. This result is shown in Figure 2A. Apparently, reaction of cyclohexene with O_3 in the presence of alcohols does lead to alkoxyhydroperoxy aldehydes, but for the cyclohexene concentrations and alcohols used in our experiments only the product of the 1-propanol reaction had sufficiently low volatility to form detectable aerosol. Experiments with cycloheptene [C_7H_{12}] and cyclooctene [C_8H_{14}] in the presence of 1-propanol yielded mass spectra (Figures 2B and 2C) in which the *m/z* 113 and 157 peaks observed for cyclohexene were shifted to *m/z* 127 and 171 and *m/z* 141 and 185, respectively. In addition, peaks appeared at *m/z* 187 and 201, 16 mass units above the *m/z* 171 and 185 peaks that are markers for the alkoxyhydroperoxy aldehydes.

To verify the presence of alkoxyhydroperoxy aldehydes and attempt to identify other compounds associated with the various peaks, I first synthesized alkoxyhydroperoxy aldehyde standards by bubbling O_3 through solutions of cyclohexene, cycloheptene, and cyclooctene in 1-propanol. This method is known to form alkoxyalkyl hydroperoxides from terminal alkenes in nearly quantitative yields[30] and was used successfully in our previous studies on 1-tetradecene.[6] For cyclooctene, the reacted solution was purified by HPLC and analyzed on-line by real-time TDPBMS. The cyclohexene and cycloheptene reaction products were too volatile to obtain sufficient signal using this approach, so solutions were atomized and analyzed by TPTD to obtain pure compound mass spectra. The solutions analyzed by TPTD showed relatively sharp, single desorption peaks at ~30−45 °C, which is the range in which the dicarboxylic acids adipic (same as hexanedioic) acid [$HO(O)C(CH_2)_4C(O)OH$] and pimelic (same as heptanedioic) acid [$HO(O)C(CH_2)_5C(O)OH$] desorb, indicating that these are reasonable temperatures for the alkoxyhydroperoxy aldehydes. HPLC separation of the cyclooctene solution also yielded one major compound.

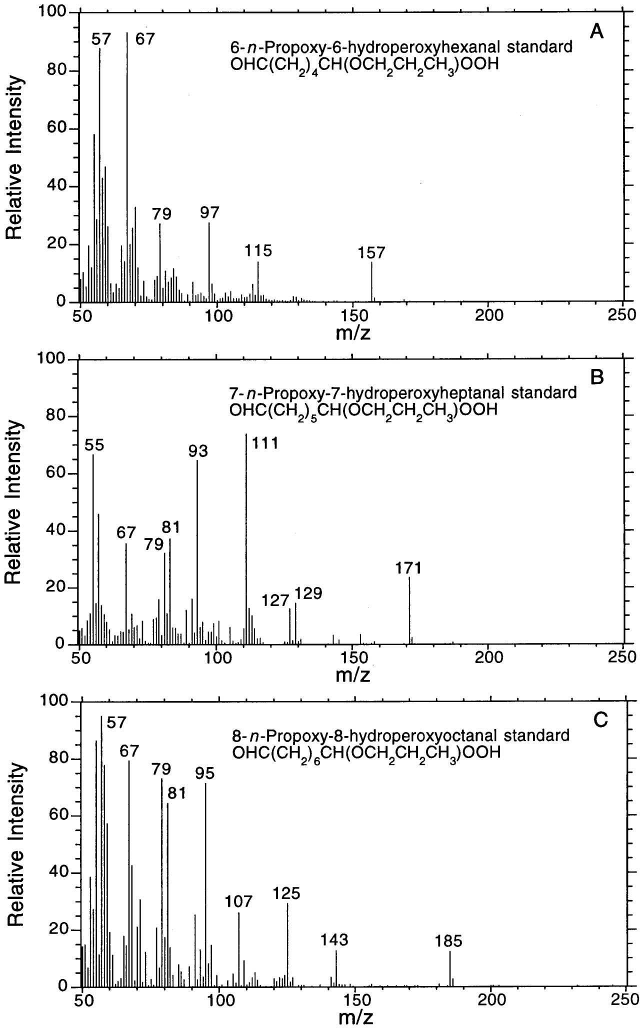
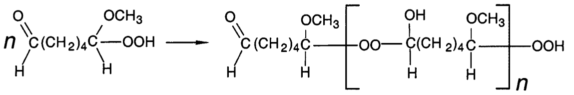


Figure 3. Mass spectra of (A) 6-*n*-propoxy-6-hydroperoxyhexanal, (B) 7-*n*-propoxy-7-hydroperoxyheptanal, and (C) 8-*n*-propoxy-8-hydroperoxyoctanal standards synthesized by bubbling O_3 through 1-propanol solutions of cyclohexene, cycloheptene, and cyclooctene, respectively. The 6-*n*-propoxy-6-hydroperoxyhexanal and 7-*n*-propoxy-7-hydroperoxyheptanal spectra were obtained using temperature-programmed thermal desorption TDPBMS to separate the compounds from residual material, and the 8-*n*-propoxy-8-hydroperoxyoctanal mass spectrum was obtained by real-time TDPBMS after purification of the solution by HPLC.

The mass spectra, which are shown in Figure 3, exhibit similar patterns. Strong high-mass peaks are present at *m/z* 157, 171, and 185 for cyclohexene, cycloheptene, and cyclooctene, respectively, corresponding to the $OHC(CH_2)_4CHOCH_2CH_2CH_3^+$, $OHC(CH_2)_5CHOCH_2CH_2CH_3^+$, and $OHC(CH_2)_6CHOCH_2CH_2CH_3^+$ ions formed by loss of 33 (HO_2) from the molecular ions. These ions subsequently lose 42 ($CH_3CH{=}CH_2$), 60 ($CH_3CH_2CH_2OH$), and 60 + 18 (H_2O) to give ions at $[M-75]^+$, $[M-93]^+$, and $[M-111]^+$, respectively. Losses of 33 and 33 + 42 were observed previously for α-isopropoxytridecyl hydroperoxide formed in the 1-tetradecene reaction.[6]

It is worth noting that the solution reaction of cyclohexene with O_3 in methanol has been studied by Bailey,[34] who concluded from elemental and infrared analysis, wet chemical analysis of methoxy groups and peroxide content, and cryoscopic molecular weight determinations, that the dried products were mixtures of $OHC(CH_2)_4CH(OCH_3)OOH$ and small peroxyhemiacetal polymers formed by intermolecular reactions of the alkoxyhydroperoxy aldehydes (R12), which could react further with methanol to form acetals by replacement of $-OH$ by $-OCH_3$. Very little polymer appears to have formed in my



$$n\,\mathrm{OHC(CH_2)_4CH(OCH_3)OOH} \longrightarrow \mathrm{OHC(CH_2)_4CH(OCH_3)}{-}\left[\mathrm{OO{-}CH(OH)(CH_2)_4CH(OCH_3)}\right]_n{-}\mathrm{OOH} \qquad \text{(R12)}$$

syntheses, since polymers would desorb at much higher temperatures than those observed here and the desorption profiles should have long tails due to thermal decomposition. The reason for this is probably that my ozonation reactions were complete in 5 s instead of 1 h, the alkene concentrations were ~0.01 M instead of ~1 M, the samples were not dried (except briefly when the aerosol was formed), and the products were analyzed immediately after synthesis. All these factors should yield a less polymerized product.

Comparison of the chamber aerosol mass spectra from reactions of cyclohexene, cycloheptene, and cyclooctene (Figure 2) with mass spectra of the alkoxyhydroperoxy aldehyde standards (Figure 3) supports the hypothesis that alkoxyhydroperoxy aldehydes are present in the particles, but also indicates that additional compounds are present that are associated with the reactions of the SCI and alcohol and are responsible for the other characteristic peaks (e.g., *m*/*z* 141 and 201 for cyclooctene). To further investigate the nature of these compounds, I performed ozonolysis experiments with cyclodecene [$C_{10}H_{18}$], which because of its lower volatility produced more aerosol than the other cyclic alkenes.

SOA Formation from Reactions of O_3 with Cyclodecene in the Presence of Alcohols, Water, and Formaldehyde. The real-time TDPBMS mass spectra of aerosol formed in the chamber after 1 and 30 min of reaction of cyclodecene with O_3 in the presence of 1-propanol and methanol are shown in Figure 4. The mass spectra of the alkoxyhydroperoxy aldehydes synthesized by the same reactions in solution and purified by HPLC are shown in Figure 5, along with mass spectra of standards of azelaic (same nonanedioic) acid [$HO(O)C(CH_2)_7C(O)OH$] and sebacic (same as decanedioc) acid [$HO(O)C(CH_2)_8C(O)OH$], which are dicarboxylic acids formed in the chamber reaction. The mass spectrum of the 10-*n*-propoxy-10-hydroperoxydecanal standard (Figure 5A) exhibits major peaks at *m*/*z* 213, 171, 153, and 135 (i.e., $[M-33]^+$, $[M-(33 + 42)]^+$, $[M-(33 + 60)]^+$, $[M-(33 + 60 + 18)]^+$) due to the same fragmentation pathways observed for the standards prepared by ozonolysis of cyclohexene, cycloheptene, and cyclooctene in 1-propanol (Figure 3), whereas the 10-methoxy-10-hydroperoxydecanal standard (Figure 5B) has major peaks at *m*/*z* 185, 153, and 135 (i.e., $[M-33]^+$, $[M-(33 + 32)]^+$, and $[M-(33 + 32 + 18)]^+$). As expected, during fragmentation the methoxyhydroperoxy aldehyde loses methanol (mass 32) instead of 1-propanol (mass 60), and no propene (mass 42) is lost. In the cyclodecene chamber reactions (Figure 4), peaks due to the alkoxyhydroperoxy aldehydes are much larger than was the case for the smaller cyclic alkenes (Figure 2), probably because of their lower volatility. Furthermore, for cyclodecene the peaks at *m*/*z* 169 and 229 in the 1-propanol reaction and at *m*/*z* 169 and 201 in the methanol reaction, which correspond to peaks observed in chamber reactions of the smaller cyclic alkenes (e.g., *m*/*z* 141 and 201 for cyclooctene with 1-propanol), increase with time relative to the alkoxyhydroperoxy aldehyde peaks.

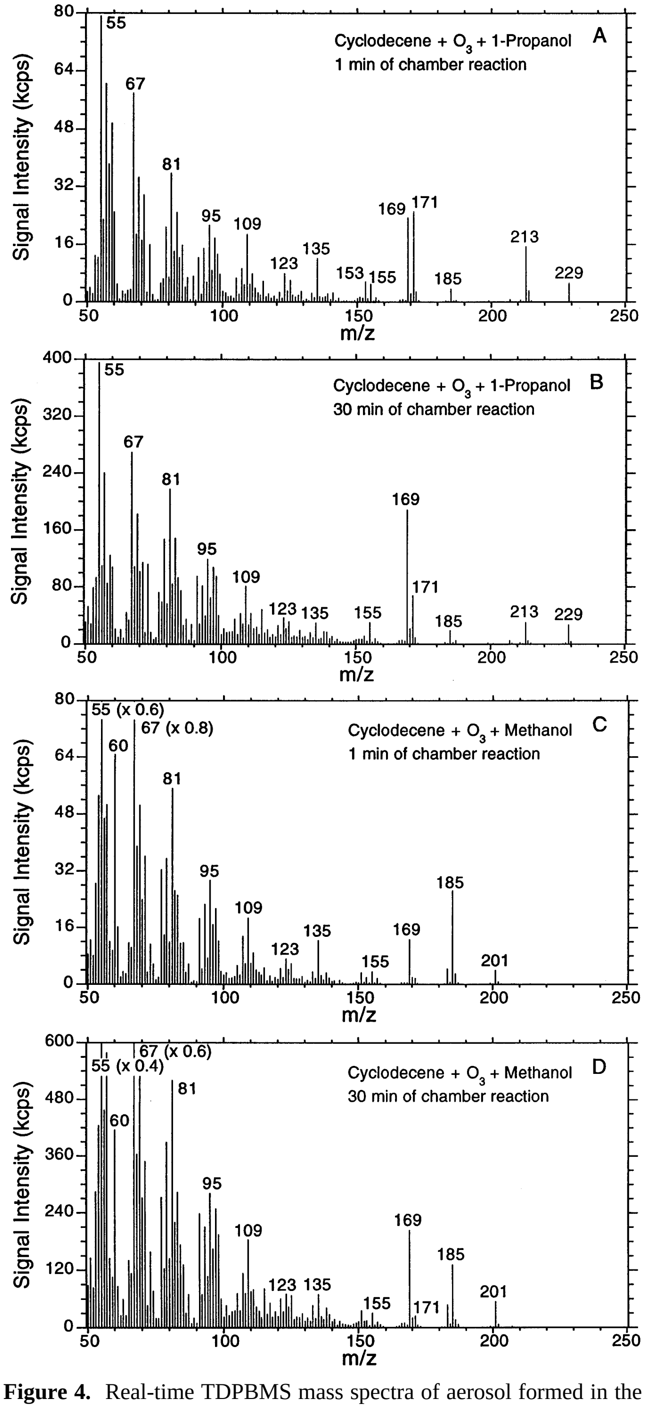


Figure 4. Real-time TDPBMS mass spectra of aerosol formed in the environmental chamber reaction of O_3 with cyclodecene in the presence of (A) 1-propanol after 1 min, (B) 1-propanol after 30 min, (C) methanol after 1 min, and (D) methanol after 30 min. The alcohol acts as an OH radical scavenger and a stabilized Criegee intermediate (SCI) scavenger.

The TPTD desorption profiles of chamber aerosol from the reaction of cyclodecene with O_3 in the presence of 1-propanol are shown in Figure 6 for selected *m*/*z* ratios. Profiles for some of the major high-mass peaks present in the 10-*n*-propoxy-10-hydroperoxydecanal standard are shown in Figure 6A. All exhibit a single, relatively sharp peak at ~50 °C, which is indicative of the presence of 10-*n*-propoxy-10-hydroperoxydecanal. The standard desorbed at ~40 °C (not shown), but this difference is not surprising because the absolute desorption temperature depends slightly on the particle matrix and sample

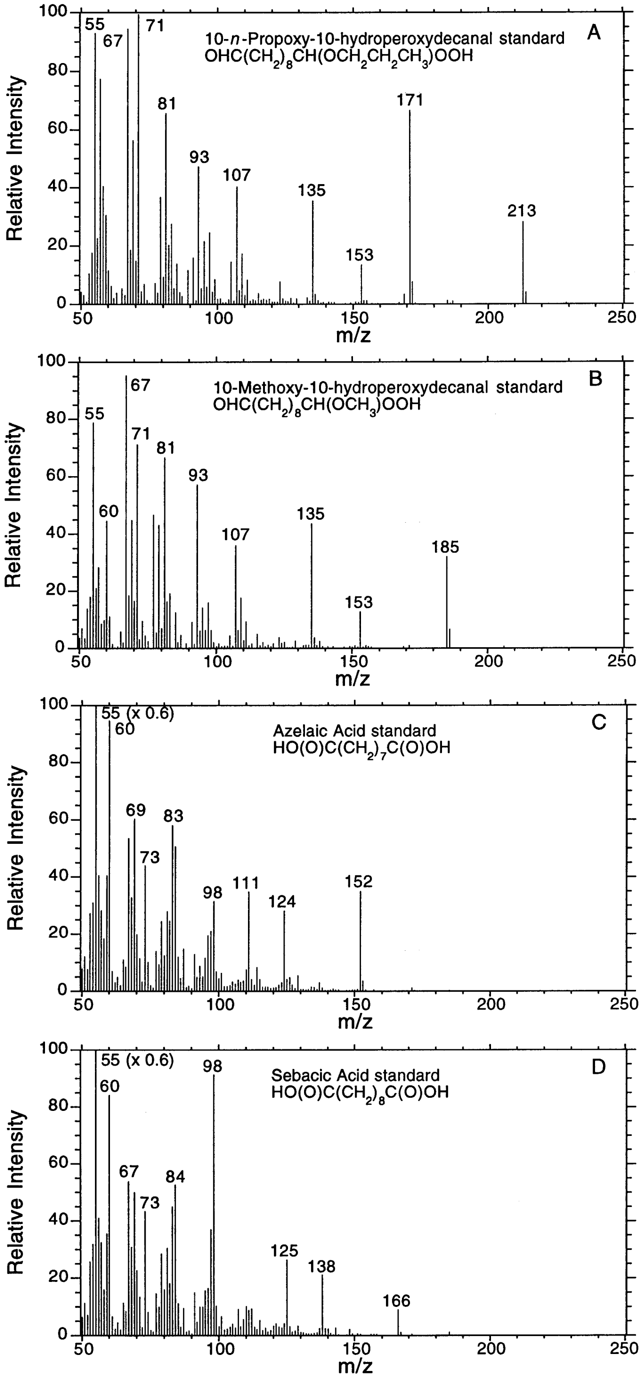


Figure 5. Real-time TDPBMS mass spectra of (A) 10-*n*-propoxy-10-hydroperoxydecanal, (B) 10-methoxy-10-hydroperoxydecanal, (C) azelaic acid, and (D) sebacic acid standards. The 10-*n*-propoxy-10-hydroperoxydecanal and 10-methoxy-10-hydroperoxydecanal standards were synthesized by bubbling O_3 through solutions of cyclodecene in 1-propanol and methanol, respectively, and then purified by HPLC. The azelaic and sebacic acids were commercially available.

size. The desorption temperature is comparable to those of azelaic acid (~43 °C) and sebacic acid (~52 °C) shown in Figure 6D. The presence of these dicarboxylic acids is not obvious from the real-time spectrum, but is apparent from the similarities in the profiles of *m*/*z* 124 and 152, and *m*/*z* 138 and 166, which are characteristic peaks in the azelaic acid (Figure 5C) and sebacic acid (Figure 5D) mass spectra, respectively. Possible mechanisms for the formation of these dicarboxylic acids have been proposed previously,[18] with the initial steps being the same as those shown above for cyclohexene (R1b, R5, R6).

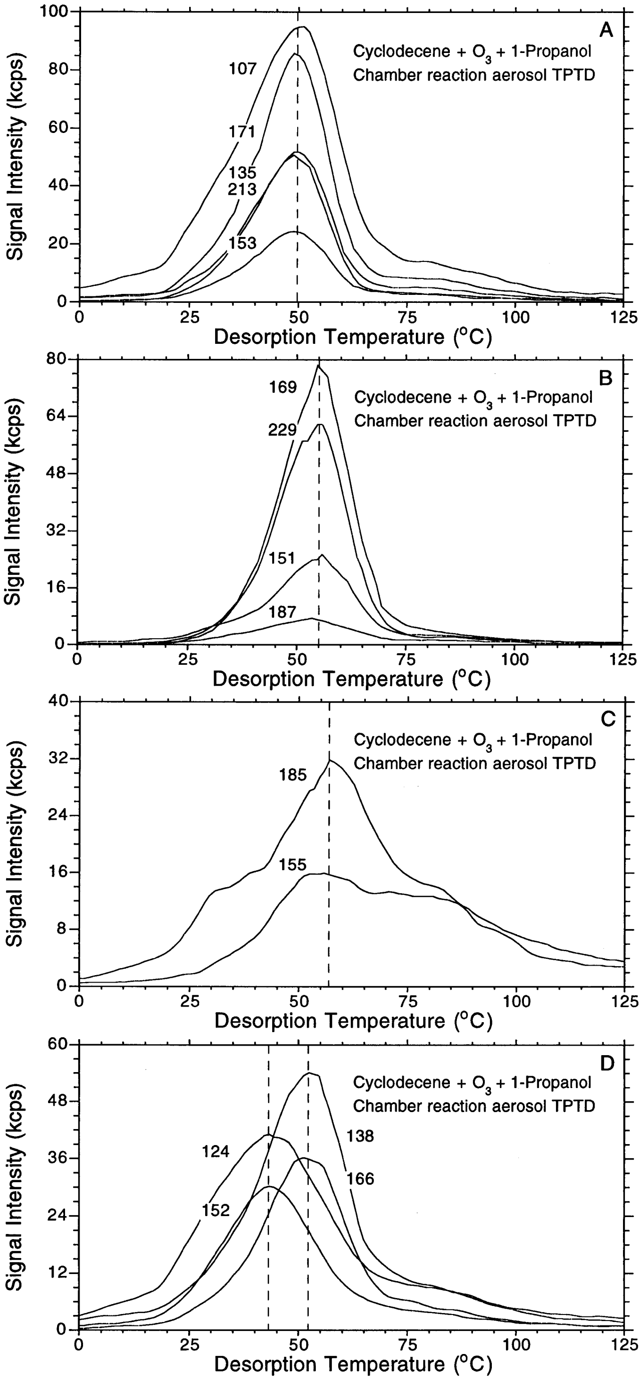


Figure 6. Temperature-programmed thermal desorption profiles of selected *m*/*z* ratios for aerosol compounds formed in the environmental chamber reaction of O_3 with cyclodecene in the presence of 1-propanol. The *m*/*z* 169 curve has been divided by a factor of 3 for easier comparison with the other curves. The 1-propanol acts as an OH radical scavenger and a stabilized Criegee intermediate (SCI) scavenger. The compounds desorb at approximately (A) 50 °C, (B) 55 °C, (C) 57 °C, and (D) 43 °C and 52 °C.

The desorption profiles of *m*/*z* 151, 169, 187, and 229 are shown in Figure 6B. The sharp, single peak in the profiles and similar peak temperatures indicate that these masses are all associated with a single compound, which is only slightly less volatile than 10-*n*-propoxy-10-hydroperoxydecanal and the dicarboxylic acids, as indicated by the peak desorption temperature of ~55 °C. The compound is apparently not polymeric material formed as in (R12), which would be expected to exhibit a much broader profile extending to higher desorption temperatures. For example, in the chamber reaction of 1-tetradecene with O_3 in the presence of methanol, the desorption peak of α-methoxytridecyl hydroperoxide was ~33 °C and that of the peroxyhemiacetal formed by (R9) was ~69 °C.[6]

The desorption profiles of *m*/*z* 155 and 185, which are mass peaks that also grew in over time relative to 10-*n*-propoxy-10-hydroperoxydecanal peaks, are shown in Figure 6C. Although the profiles have maxima close to 55 °C, they are much broader than those in Figure 6B and have long tails that extend to higher temperatures. These masses are apparently associated with a number of compounds, which may or may not have been formed by pathways involving reactions of SCI with alcohols. In an effort to evaluate the various contributions to the *m*/*z* 155 and 185 peaks, as well as those at *m*/*z* 169 and 171, chamber reactions of O_3 with cyclodecene in the presence of the SCI scavengers water and formaldehyde were performed under conditions similar to those used in the alcohol reactions. On the basis of my previous study,[18] the reactions of these scavengers with SCI should lead to products that are too volatile to form aerosol, and thus will not contribute to the mass spectrum. Reaction with water should initially yield a hydroxyhydroperoxy aldehyde that decomposes to a volatile aldehyde or carboxylic acid as in R7a,b), while reaction with formaldehyde should yield a volatile C_{11} secondary ozonide. The real-time TDPBMS mass spectra obtained after 20 min of reaction are shown in Figures 7A and 7B. The spectra are similar, indicating that the products of the reactions of cyclodecene SCI with water and formaldehyde probably do not contribute significantly to the aerosol, and that these mass spectra are representative of compounds formed by other pathways. In addition, the high-mass peaks at *m*/*z* 155, 169, 171, and 185 correspond to the four high-mass peaks observed previously[18] for the reactions of O_3 with cyclohexene in the presence of water and formaldehyde, shifted by 56 mass units, and for cycloheptene and cyclooctene in the presence of water (no formaldehyde reaction was performed), shifted by 42 and 28 mass units, respectively. Although the compounds associated with this series of peaks have not yet been definitively identified, a variety of evidence was presented supporting the hypothesis that they are due to diacyl peroxides [^{1}RC(O)OO(O)CR^2] formed from association reactions of the same acyl peroxy radicals that lead to dicarboxylic acids.

Comparing the intensities of *m*/*z* 155, 169, 171, and 185 in the mass spectra from reactions of cyclodecene and alcohols (Figure 4) with those in the mass spectra of the water and formaldehyde reactions (Figure 7A,B) shows that the peaks that are clearly dominated by contributions from the SCI reactions are *m*/*z* 169 and 171 for 1-propanol and *m*/*z* 169 and 185 for methanol. Contributions from reactions of SCI with alcohols are more difficult to determine for *m*/*z* 155 and 185 for 1-propanol and *m*/*z* 155 and 171 for methanol because the intensities are similar to those of the corresponding peaks in the water and formaldehyde reaction mass spectra. As an example, Figure 7C shows the relative signal for (*m*/*z* 169)/(*m*/*z* 138) during the first 20 min of the 1-propanol, methanol, water, and formaldehyde reactions. The *m*/*z* 138 peak is a marker for sebacic acid, which is thought to be formed through pathways that do not involve association reactions of SCI and so should be formed in similar amounts in all reactions. The signal ratios for the water and formaldehyde reactions are essentially the same, with both slowly increasing over time. The signal ratios for the 1-propanol and methanol reactions are much larger, with both slowly decreasing over time. The similarity in the water and formaldehyde curves are indicative of aerosol formation that is not influenced by association reactions of SCI with these scavengers, whereas the 1-propanol and methanol reactions with SCI lead to additional products that contribute significant signal at *m*/*z* 169, thus increasing the signal ratios.

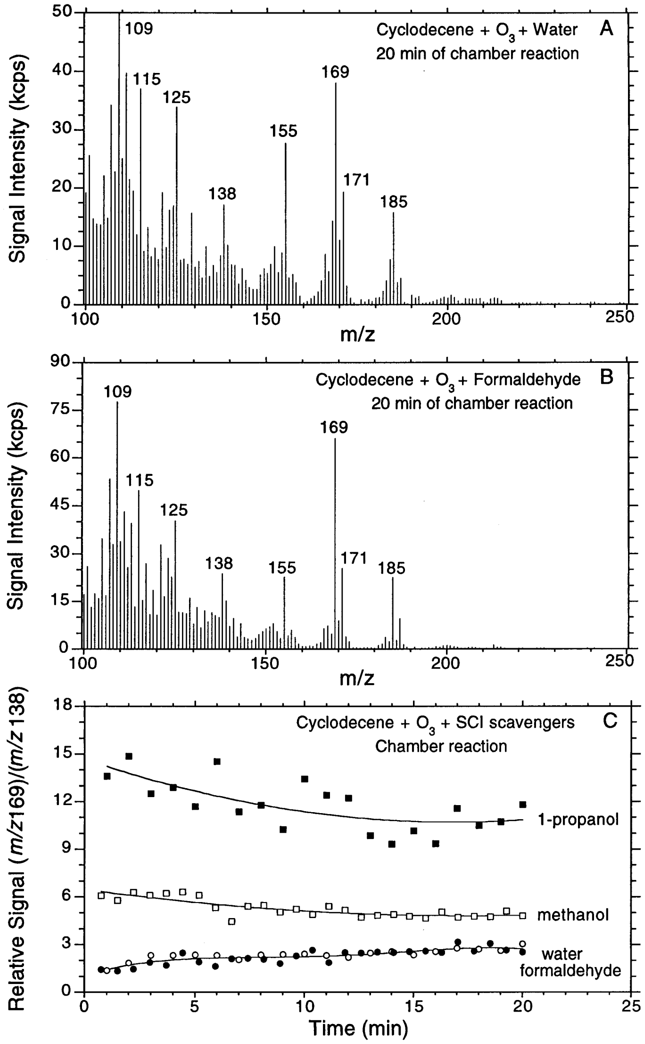


Figure 7. Real-time TDPBMS mass spectra of aerosol formed in the environmental chamber after 20 min of reaction of O_3 with cyclodecene in the presence of cyclohexane and (A) water and (B) formaldehyde. The cyclohexane acts as an OH radical scavenger and the water and formaldehyde act as stabilized Criegee intermediate (SCI) scavengers. (C) Ratio of (*m*/*z* 169)/(*m*/*z* 138) signals for the reactions of O_3 with cyclodecene in the presence of the SCI scavengers 1-propanol (filled squares), methanol (open squares), water (filled circles), and formaldehyde (open circles). The *m*/*z* 138 peak is a marker for sebacic acid.

On the basis of the evidence presented above, I propose that for the reaction of cyclodecene in the presence of 1-propanol the compound that desorbs at ~55 °C is a cyclic peroxyhemiacetal, 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane, which forms from 10-*n*-propoxy-10-hydroperoxydecanal by an intramolecular reaction of the hydroperoxyl and carbonyl groups. The mechanism of formation of both peroxides is shown in Figure 8. Initially, O_3 adds to the cyclodecene double bond to form an excited primary ozonide, which decomposes to an excited Criegee intermediate (syn or anti conformation). An excited anti Criegee intermediate is stabilized by collisions with air and reacts with 1-propanol to form 10-*n*-propoxy-10-hydroperoxydecanal. The 10-*n*-propoxy-10-hydroperoxydecanal then cyclizes to 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane. The reaction is similar to that observed previously for 1-tetradecene (R9),[6] except that the peroxyhemiacetal is formed through an intramolecular, rather than intermolecular, reaction.

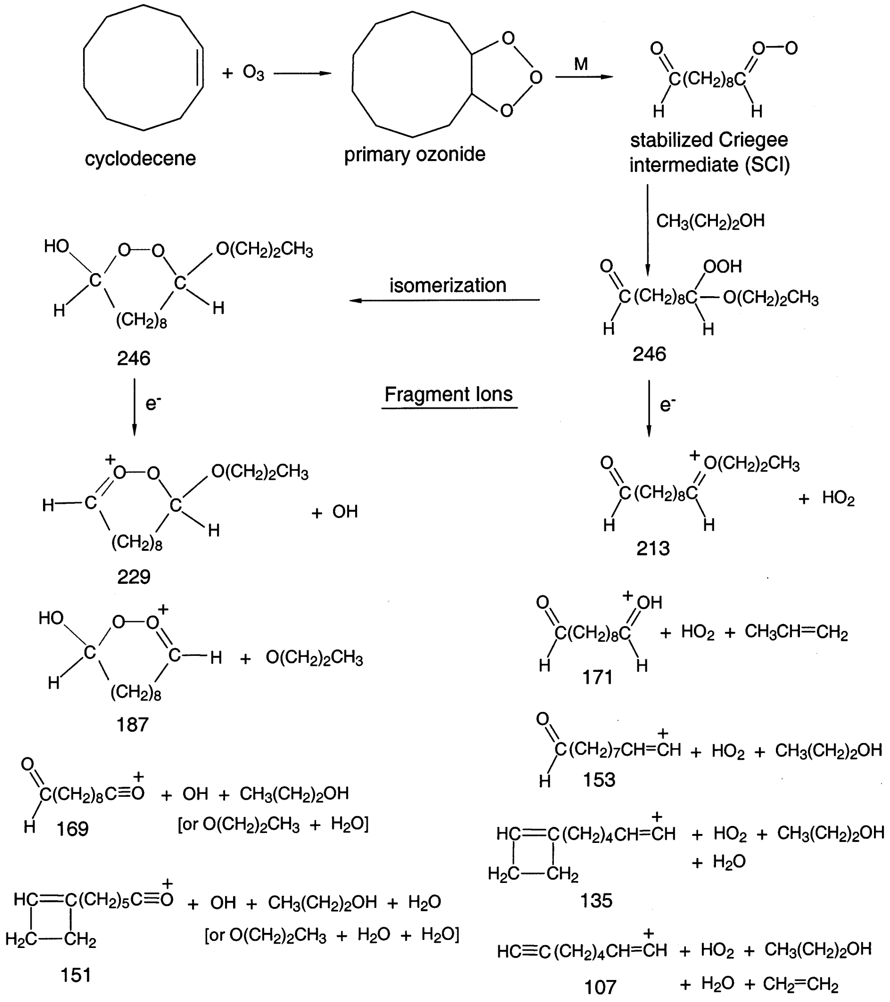


Figure 8. Proposed mechanism for the formation of 10-*n*-propoxy-10-hydroperoxydecanal and 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane products from the reaction of O_3 with cyclodecene in the presence of 1-propanol, and proposed electron ionization fragmentation pathways for the formation of selected mass spectral peaks.

The reaction is also similar to that observed for 4-hydroxy-4-methyl-5-hexenal formed in the gas-phase reaction of O_3 with the monoterpene derivative, linalool.[35] There the carbonyl group reacted intramolecularly with a hydroxyl group to form a stable hemiacetal, 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran.

The proposed electron ionization fragmentation pathways for forming some of the major high-mass peaks in the mass spectra of 10-*n*-propoxy-10-hydroperoxydecanal and 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane are also shown in Figure 8. The loss of HO_2 and $CH_3CH{=}CH_2$ shown for 10-*n*-propoxy-10-hydroperoxydecanal was also observed for α-isopropoxytridecyl hydroperoxide formed in the 1-tetradecene reaction,[6] and loss of $CH_3(CH_2)_2OH$, H_2O, and $CH_2{=}CH_2$ are common pathways for ions containing $-O(CH_2)_2CH_3$, $-CHOH$, and $-CHO$ groups.[36] The mass spectrum of 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane is expected to have peaks due to loss of OH and $O(CH_2)_2CH_3$, as is observed in mass spectra of cyclic ethers[36] including 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran formed from ozonolysis of linalool.[35] Loss of $CH_3(CH_2)_2OH$ from the *m*/*z* 229 ion is also expected because of the energetically favorable six-membered ring transition state for $CH_3(CH_2)_2OH$ formation and the high stability of the *m*/*z* 169 acylium ion, and loss of H_2O is common for aldehydes.[36]

Mechanism of Alkoxyhydroperoxy Aldehyde Cyclization. To further investigate the mechanism of formation of 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane, I performed an experiment in which the products formed by bubbling O_3 through a solution of cyclodecene in 1-propanol were atomized into the environmental chamber and the aerosol was monitored by TDPBMS. The real-time mass spectrum obtained at the end of the 15 min it took to add the aerosol to the chamber is shown in Figure 9A, and the mass spectrum obtained after 45 min is shown in Figure 9B. The spectra are essentially identical and are dominated by peaks from 10-*n*-propoxy-10-hydroperoxydecanal, which is the major product of the solution reaction. There is a small peak at *m*/*z* 169 and a barely detectable peak at *m*/*z* 229 that are apparently due to 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane. The only change in the mass spectrum over 30 min is a slight decrease in overall signal intensity due to particle losses to the chamber walls. These are very different from the mass spectra obtained from the gas-phase chamber reaction of cyclodecene, where *m*/*z* 169 and 229 were strong peaks in the first minute of reaction (Figure 4A) and then grew in significantly relative to the 10-*n*-propoxy-10-hydroperoxydecanal peaks over the next 30 min (Figure 4B).

One explanation for this difference is that the cyclization reaction only occurs in the gas phase, and that the 10-*n*-propoxy-10-hydroperoxydecanal added to the chamber as an aerosol did not form sufficient vapor to allow a significant amount of cyclization to occur. The small amount of 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane that is present in the initially atomized aerosol, which does not change over time, might have formed in the headspace of the bubbler during ozonolysis and then dissolved into the solution. The almost constant mass

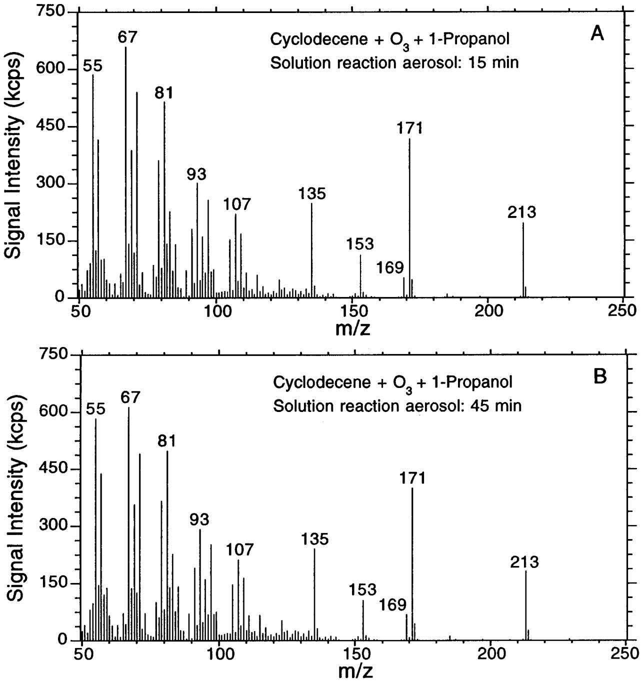


Figure 9. Real-time TDPBMS mass spectra of aerosol formed by bubbling O_3 through a solution of cyclodecene in 1-propanol and then atomizing the solution into the environmental chamber. The mass spectra are for aerosol (A) analyzed at the end of the 15 min period during which aerosol was added to the chamber and (B) analyzed 45 min after beginning to add aerosol.

spectral signal in Figures 9A and 9B shows that there was little net evaporation of 10-*n*-propoxy-10-hydroperoxydecanal particles during 30 min. The fraction of the particle mass that entered the gas phase during this period can be estimated using evaporation rate theory[37] and the vapor pressure of 10-*n*-propoxy-10-hydroperoxydecanal. The desorption temperature for this compound is similar to that of sebacic acid, which has a vapor pressure at 25 °C of 7×10^{-8} Pa,[38] so this value should be appropriate for 10-*n*-propoxy-10-hydroperoxydecanal. The calculated lifetime for a 0.2 μm particle evaporating into air in the absence of vapor is ~100 h, which corresponds to evaporation of ~1% of the particle mass during the 45 min period that particles are present in the chamber. For a particle mass concentration of ~1700 μg m^{-3} (measured by the SMPS) this would yield a vapor concentration of ~17 μg m^{-3}, which corresponds to a partial pressure of ~2×10^{-4} Pa. Since this value is much higher than the saturation vapor pressure, the net evaporation rate will be slower than the ~1% h^{-1} calculated on the assumption of zero partial pressure and will depend on the rate of diffusion and loss of vapor to the chamber walls. Because the equilibrium is a dynamic one, however, the evaporation rate calculated in the absence of vapor is the proper value to use to estimate the rate of particle−vapor exchange. It would then be expected that ~1% of the 10-*n*-propoxy-10-hydroperoxydecanal entered the gas phase during the experiment, which is too little to form measurable amounts of cyclic product.

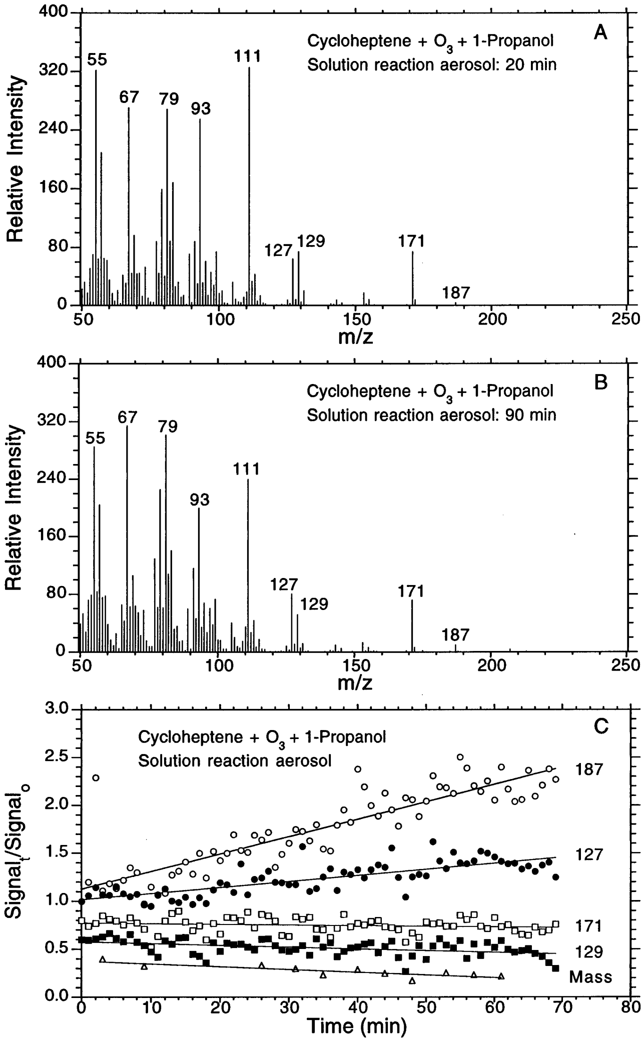


Figure 10. Real-time TDPBMS mass spectra of aerosol formed by bubbling O_3 through a solution of cycloheptene in 1-propanol and then atomizing the solution into the environmental chamber. The mass spectra are for aerosol analyzed (A) at the end of the 20 min period during which aerosol was added to the chamber and (B) 90 min after beginning to add aerosol. (C) Ratio of signal measured at a given time (Signal$_t$) to signal measured at the end of the 20 min period during which aerosol was added to the chamber (Signal$_o$). Ratios are given for *m*/*z* 127, 129, 171, and 187, and for particle mass concentrations measured by SMPS. The curves have been offset vertically in order to improve the clarity of the presentation.

Although this result supports the hypothesis that the cyclization reaction only occurs in the gas phase, it does not answer the question of whether the reaction occurs under thermal conditions or requires excess energy that would be available in the initial reaction of the SCI with 1-propanol. I therefore repeated the experiment described above with 7-*n*-propoxy-7-hydroperoxyheptanal formed from the solution reaction of O_3 with cycloheptene in 1-propanol. This compound is more volatile than 10-*n*-propoxy-10-hydroperoxydecanal and so might produce enough cyclic product for detection if the reaction can occur under thermal conditions. The real-time mass spectrum obtained at the end of the 20 min it took to add the aerosol to the chamber is shown in Figure 10A and the mass spectrum obtained after 90 min is shown in Figure 10B. The spectra are both dominated by peaks from 7-*n*-propoxy-7-hydroperoxyheptanal (Figure 3B), especially initially, but peaks are also present at *m*/*z* 127 and 187, which increase over time. These are the peaks expected for the cyclic reaction product 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclononane, although *m*/*z* 127 is also present in 7-*n*-propoxy-7-hydroperoxyheptanal. Figure 10C shows the mass spectral signal for *m*/*z* 127, 129, 171, and 187 measured for 70 min after adding the atomized aerosol to the chamber. Also shown is the particle mass concentration measured by the SMPS. The curves have each been normalized to the initial signal and offset vertically for clarity. The signals for *m*/*z* 129 and 171, which are associated with 7-*n*-propoxy-7-hydroperoxyheptanal, and the particle mass all decrease over time at

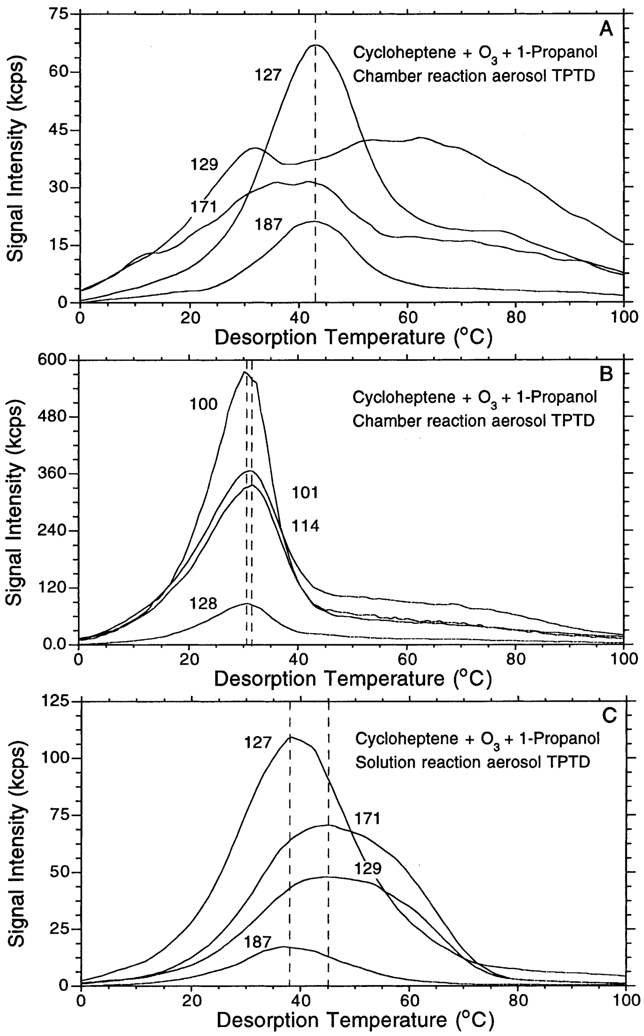


Figure 11. Temperature-programmed thermal desorption profiles of selected *m/z* ratios for (A or B) aerosol formed in the environmental chamber reaction of O_3 with cycloheptene in the presence of 1-propanol, which acts as an OH radical and stabilized Criegee intermediate (SCI) scavenger, and (C) aerosol formed by bubbling O_3 through a solution of cycloheptene in 1-propanol and then atomizing the solution into the environmental chamber. The atomized aerosol was collected for analysis during the 200−230 min period after adding aerosol to the chamber, and the aerosol formed in the chamber reaction was collected for analysis during the 30−60 min period of reaction. In (A), the *m/z* 127 curve was divided by a factor of 2 and the *m/z* 171 curve was multiplied by a factor or 4 for easier comparison with the other curves.

rates of approximately 13%, 4%, and 17% h^{-1}. The fluctuations in the data are sufficient to explain the differences in these values. The rates of decrease are similar to typical particle deposition rates in the chamber, which are $\sim$15% h^{-1}.[20] On the other hand, the signals for *m/z* 127 and 187 both increase over time, indicating that the compound associated with these peaks is being formed by reaction from 7-*n*-propoxy-7-hydroperoxyheptanal. Because the absolute intensities of the *m/z* 127 and 187 peaks increase, as well as the intensities relative to *m/z* 129 and 171, the explanation cannot be that 7-*n*-propoxy-7-hydroperoxyheptanal is simply evaporating from the particles faster than 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclononane. The ratio of the increase in the absolute *m/z* 127 and *m/z* 187 signals is $\sim$6, which is close to the ratio of peak intensities obtained from the thermal desorption profiles for atomized aerosol shown in Figure 11C. The vapor pressure of 7-*n*-propoxy-7-hydroperoxyheptanal should be slightly less than that of adipic acid, which has a slightly lower desorption temperature (Figure 11B) and a vapor pressure at 25 °C of 8×10^{-6} Pa.[38] This value yields a calculated particle−gas exchange rate of $\sim$100% hr^{-1}. The fraction of the 7-*n*-propoxy-7-hydroperoxyheptanal mass exchanged with the vapor in 1 h should then be much more than for 10-*n*-propoxy-10-hydroperoxydecanal, and probably on the order of 10% or more. This is consistent with the apparent observation of a cyclization reaction in the case of 7-*n*-propoxy-7-hydroperoxyheptanal but not 10-*n*-propoxy-10-hydroperoxydecanal.

Thermal desorption profiles of aerosol formed in the environmental chamber reaction of O_3 with cycloheptene in the presence of 1-propanol and collected for analysis during the 30−60 min period of reaction are shown in Figures 11A and 11B. The profiles for *m/z* 127 and 187 are indicative of a single compound, which supports the assignment of *m/z* 127 and 187 to 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclononane. Although they cannot be resolved, the compounds associated with *m/z* 100 and 128 and *m/z* 101 and 114 are probably adipic acid and pimelic acid (mass spectra not shown), respectively, which correspond to the azelaic and sebacic acids formed in the cyclodecene reaction. The cyclic product, 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclononane, appears to be slightly less volatile than the dicarboxylic acids, as was the case in the cyclodecene reaction. The cyclic peroxyhemiacetal and dicarboxylic acids formed in the cycloheptene reaction desorb at temperatures $\sim$10−20 °C lower than those formed in the cyclodecene reaction, as expected for compounds with 3 less CH_2 units. The profiles for *m/z* 129 and 171 are very broad and are clearly associated with more than one compound, which probably includes 7-*n*-propoxy-7-hydroperoxyheptanal and compounds formed by pathways that may or may not involve reactions of SCI with 1-propanol.

The desorption profiles for *m/z* 127 and 187 for the atomized cycloheptene reaction aerosol (Figure 11C) are also relatively sharp with a single peak at $\sim$38 °C, which is close to the $\sim$43 °C peak for the cyclic compound formed in the gas-phase O_3 reaction (Figure 11A). The desorption profiles for *m/z* 129 and 171 for the atomized aerosol (Figure 11C) have a single broad peak centered at $\sim$50 °C, which is $\sim$7 °C higher than 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclononane. The broad profile and higher than expected desorption temperature (the corresponding alkoxyhydroperoxy aldehyde formed in the cyclodecene reaction had a sharper profile and desorbed slightly before the cyclic peroxyhemiacetal) may indicate the onset of 7-*n*-propoxy-7-hydroperoxyheptanal polymerization. In our studies of 1-tetradecene, the mass spectra of the alkoxyalkyl hydroperoxide and peroxyhemiacetal were quite similar and peroxyhemiacetal formation probably occurred at the particle surface rather than in the gas phase.[6] Because there was no evidence for polymerization in the cyclodecene reaction, it may be that 7-*n*-propoxy-7-hydroperoxyheptanal particles are liquid with sufficient molecular mobility for polymerization, whereas 10-*n*-propoxy-10-hydroperoxydecanal particles are solid and therefore less reactive. The evidence for polymerization is not definitive, although one would expect that such reactions could occur. In general, the extent of polymerization should be determined by the phase of the particle and the volatility of the alkoxyhydroperoxy aldehydes, since formation of cyclic peroxyhemiacetals in the gas phase will prevent polymerization.

Conclusions

In this study, the products and mechanisms of SOA formation from reactions of O_3 with cyclohexene, cycloheptene, cyclooctene, and cyclodecene in the presence of alcohols were investigated using a thermal desorption particle beam mass spectrometer. Peroxide products formed through association reactions of SCI with alcohols were observed, in contrast to my previous study on reactions of cyclohexene, cycloheptene, and cyclooctene with O_3 in the presence of water.[18] In that study, the pathways to aerosol formation appeared to occur solely through isomerization and decomposition reactions of Criegee intermediates with no contributions from association reactions involving SCI. The initial products of the reactions of alcohols with SCI formed from the cyclic alkenes studied here are alkoxyhydroperoxy aldehydes, which have been identified by comparison of aerosol mass spectra with those of synthesized standards. The hydroperoxyl and carbonyl groups subsequently undergo an intramolecular reaction to form a cyclic peroxyhemiacetal. For example, in the reaction of O_3 with cyclodecene in the presence of 1-propanol, the product of the reaction of the SCI with 1-propanol is 10-*n*-propoxy-10-hydroperoxydecanal, which then isomerizes to 1-hydroxy-4-*n*-propoxy-2,3-dioxacyclododecane. Experiments performed by monitoring reactions of alkoxyhydroperoxy aldehyde standards added to the chamber indicate that the cyclization reaction occurs in the gas phase, but apparently not in the particle phase, and occurs under thermal conditions. In our previous study of the reactions of O_3 with the terminal alkene 1-tetradecene in the presence of alcohols, the major aerosol products were alkoxyalkyl hydroperoxides,[6] which cannot isomerize because they do not contain a carbonyl group. Instead, they formed peroxyhemiacetals through intermolecular reactions with the aldehyde coproducts of excited Criegee intermediates formed when the primary ozonide decomposes. This reaction apparently occurred on the particle surface rather than in the gas phase. In contrast to this behavior, the alkoxyhydroperoxy aldehydes formed in the present study appear to undergo little, if any, intermolecular reaction to form dimers or polymeric peroxyhemiacetals. This may be because the particles are solid (the actual phase is unknown), which limits molecular mobility and therefore reactivity, and because molecules that enter the gas phase cyclize before they can adsorb onto a particle surface and react with another molecule.

The contribution of the products of association reactions of SCI with alcohols to SOA mass could not be quantified in this study because standards for the cyclic peroxyhemiacetals could not be easily synthesized. As an estimate, however, if we make the following assumptions: the molar yields of SCI for all the cyclic alkenes studied are similar to that of cyclohexene and cycloheptene (both ∼3%),[33] the products of SCI association reactions condense completely into aerosol, the total molar yield of aerosol from other pathways is similar to that of cyclohexene (∼9%),[39] and the molecular weights of all SOA compounds are similar, then products of SCI-alcohol reactions might comprise ∼25% of the SOA mass. The remaining mass should be contributed by products of isomerization and decomposition reactions, such as dicarboxylic acids.

In the atmosphere, the concentrations of alcohols are generally too low to allow them to compete with water in reactions with SCI.[15,20] Formation of alkoxyhydroperoxides is therefore not expected to be significant. Formation of hydroxyhydroperoxy aldehyde products from the reaction of water with SCI formed from cyclic alkenes also appears to be unimportant, since these compounds are unstable and decompose to aldehydes and hydrogen peroxide or to water and carboxylic acids.[4,17,19,24] This behavior contrasts with that of the hydroxyalkyl hydroperoxides formed from reactions of acyclic alkenes, which are sufficiently stable to have been observed among gas-phase and aerosol reaction products.[21−23] The only difference between some of these compounds is the presence of a carbonyl group in the unstable hydroxyhydroperoxy aldehydes, which may mean that cyclization can facilitate decomposition. In recent studies on gas-phase hydroxycarbonyls, which are major products of many atmospheric reactions, intramolecular reactions between hydroxyl and carbonyl moieties have been observed that lead to stable[35] and unstable[40,41] cyclic hemiacetals, with the latter decomposing to a cyclic alkene (i.e., a furan) through loss of water. Recent studies have also indicated that hemiacetals formed through intermolecular, acid-catalyzed particle-phase reactions between alcohols and aldehydes may be an important mechanism for forming SOA.[7]

The results of this study help to provide a more cohesive picture of the types of products that can form from reactions of O_3 with alkenes, which is important for understanding basic reaction mechanisms and especially the particular reactions that might lead to low-volatility compounds that form SOA. This information is also valuable for interpreting the results of laboratory experiments, which often employ alcohols as OH radical scavengers and use elevated alkene concentrations (relative to ambient levels) that may lead to concentrations of SCI scavengers sufficient to compete with water.[20] There are many other interesting unanswered questions about the reactions of O_3 with cyclic and acyclic alkenes, involving both gas-phase and heterogeneous chemistry. Studies are currently underway in our lab to address some of these questions by drawing from the insights gained in this and other investigations of alkene−O_3 chemistry.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant ATM-9816610. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Science Foundation (NSF). I also thank Roger Atkinson for helpful discussions.

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