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Evidence for Low-Volatility Diacyl Peroxides as a Nucleating Agent and Major Component of Aerosol Formed from Reactions of O_3 with Cyclohexene and Homologous Compounds

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Reactions of cyclic alkenes and O_3 are known to form significant quantities of aerosol, but the chemical mechanism and complete identity of the products has not been established. In this study, a thermal desorption particle beam mass spectrometer is used to investigate the ozonolysis of cyclohexene and some of its structural homologues, including cyclopentene, cycloheptene, and cyclooctene, in humid air. Dicarboxylic acids, which are the lowest volatility compounds previously identified in aerosol formed from this reaction, are also observed here. But in addition, the thermal desorption behavior of the aerosol indicates that compounds less volatile than dicarboxylic acids are present. On the basis of mass spectra and desorption behavior of the aerosol and standard compounds, and chemical probe experiments, it is proposed that these compounds are diacyl peroxides. A reaction mechanism is presented to explain the formation of diacyl peroxides, as well as dicarboxylic acids. These results may have important implications for understanding the potential role of organic compounds in nucleation and growth of atmospheric aerosol particles.

Introduction

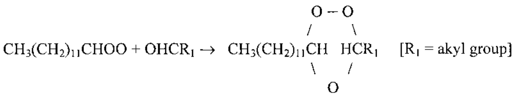
Cyclic alkenes are an important component of the anthropogenic and biogenic emissions of volatile organic compounds (VOCs) to the atmosphere.[1] Their gas phase chemistry has been studied by a number of investigators, and certain aspects are relatively well understood, especially with regards to kinetics and some of the products and mechanisms of reactions with OH and NO_3 radicals, and O_3.[1,2] Recently, increasing attention has been given to the chemistry of secondary aerosol formation from these compounds.[3−5] The focus has been primarily on the cyclic monoterpenes, such as α- and *β*-pinene, because of their large contribution to biogenic VOC emissions and their importance to the global aerosol.[6] But despite these efforts, current understanding of the chemical mechanisms by which cyclic alkenes are transformed in the atmosphere, especially to condensable products, is incomplete. Improved knowledge of this chemistry is important for understanding the role of these compounds in the formation of secondary organic aerosol, and their potential impact on global climate, atmospheric chemistry, visibility, and human health.[7,8]

One important observation from past studies is that for a number of cyclic alkenes the major pathway to aerosol formation appears to involve reaction with O_3,[9,10] rather than with the other important daytime oxidant, OH radicals. Furthermore, a significant fraction of the aerosol formed in laboratory studies of cyclic alkene-O_3 reactions is reported to be composed of dicarboxylic acids.[3−5] Because they are the lowest volatility products yet identified from these reactions, and have been found in particles collected from forested areas,[11,12] it is thought that dicarboxylic acids may be important in atmospheric nucleation and growth of new particles.[13] Although there is no generally accepted reaction mechanism for the formation of dicarboxylic acids from cyclic alkenes and O_3 in the absence of OH radicals, two slightly different mechanisms have recently been proposed for reactions of α- and *β*-pinene and their structural analogues.[13−15]

The gas-phase O_3 chemistry of linear alkenes appears to be simpler than that of the cyclic alkenes, and has been thoroughly investigated for small molecules such as ethene.[16] We have studied aerosol formation from reactions of O_3 with the linear alkene, 1-tetradecene,[17,18] using a thermal desorption particle beam mass spectrometer (TDPBMS) to analyze the aerosol composition.[19,20] It was determined that the major pathway to aerosol involves reactions of stabilized C13 Criegee intermediates with aldehydes and acidic compounds such as water, alcohols, and carboxylic acids. The reaction scheme for aerosol formation is

$$CH_3(CH_2)_{11}CH{=}CH_2 + O_3 \rightarrow [CH_3(CH_2)_{11}CHOO]^* + HCHO \quad (1)$$

$$[CH_3(CH_2)_{11}CHOO]^* + M \rightarrow CH_3(CH_2)_{11}CHOO + M\ [M = N_2, O_2] \quad (2)$$



$$CH_3(CH_2)_{11}CHOO + OHCR_1 \rightarrow CH_3(CH_2)_{11}\overset{O-O}{\underset{O}{CH\quad HCR_1}}\quad [R_1 = \text{akyl group}] \quad (3)$$

$$CH_3(CH_2)_{11}CHOO + HOR_2 \rightarrow CH_3(CH_2)_{11}CH(OR_2)OOH\quad [R_2 = H, \text{alkyl, or acyl group}] \quad (4)$$

$$CH_3(CH_2)_{11}CH(OR_2)OOH + OHCR_1 \rightarrow CH_3(CH_2)_{11}CH(OR_2)OOCH(OH)R_1 \quad (5)$$

Initially, O_3 adds to the double bond to form an excited primary ozonide, which rapidly decomposes to formaldehyde and an excited C13 Criegee intermediate, $[CH_3(CH_2)_{11}CHOO]^*$ (reaction 1). The Criegee intermediate is stabilized by collisions with air (reaction 2) and then reacts with an aldehyde to form a

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secondary ozonide (reaction 3), or with an acidic compound to form a hydroperoxide (reaction 4). The hydroperoxides can subsequently react with aldehydes (apparently heterogeneously) to form lower volatility peroxyhemiacetals (reaction 5). These types of compounds have not been identified previously in similar studies because they decompose, typically to carboxylic acids and aldehydes, when analyzed by gas chromatography−mass spectrometry (GC−MS), the most commonly used method for organic aerosol analysis.

Because of the importance of cyclic alkene-O_3 reactions in atmospheric chemistry, and as an extension of our work on linear alkenes, we have used the TDPBMS to investigate the ozonolysis of cyclohexene and some of its structural homologues, including cyclopentene, cycloheptene, and cyclooctene. These simple model compounds provide a useful introduction into the aerosol chemistry of cyclic alkenes. The results are consistent with other studies, in that dicarboxylic acids are identified as a major aerosol component. More importantly, however, we also find evidence for the presence of compounds that have not been reported previously, and which have lower vapor pressures than dicarboxylic acids. On the basis of the evidence presented here, we propose that these compounds are diacyl peroxides [$R_1C(O)OO(O)CR_2$; R_1 and $R_2 = (CH_2)_nCHO$ or $(CH_2)_mC(O)OH$], and that that they are responsible for nucleation and a significant fraction of the aerosol mass in these systems. We also present a chemical mechanism to explain the formation of diacyl peroxides and dicarboxylic acids.

Experimental Section

Materials. Cyclopentene, cyclohexene, cycloheptene, cyclooctene, glutaric acid, adipic acid, and 2-oxoadipic acid were obtained from Aldrich Chemical, Inc., and 3-hydroxy-3-methylglutaric acid and succinyl peroxide from City Chemical LLC. HPLC grade cyclohexane, methanol, and 1-propanol 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[19] and temperature-programmed thermal desorption (TPTD)[20] are presented elsewhere. Aerosol is sampled into the TDPBMS through a 100 μm orifice, which maintains the flow at 0.075 L/min and reduces the pressure from atmospheric to 300 Pa. Particles then enter a tube containing a series of aerodynamic lenses,[21,22] which focus the particles into a narrow, low-divergence particle beam that transports ~0.02−0.5 μm particles from atmospheric pressure into the high-vacuum chamber with near-unit efficiency. After exiting the aerodynamic lens, particles pass through two flat-plate skimmers separating three differentially pumped chambers and enter the detection chamber where the pressure is 10^{-5} Pa. 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 vaporizer that is either resistively heated continuously at 165 °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 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 cryogenically cooled vaporizer. The sample was desorbed by heating at a linear ramp rate of ~2 °C/min from ~0−100 °C, while mass spectra were continuously recorded. During TPTD the aerosol components desorb according to their 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.[17,20,23]

Because particles are exposed to subsaturated air inside the TDPBMS, sufficiently volatile compounds may evaporate prior to analysis. Previous calculations and experiments with compounds of known vapor pressures indicate that particulate compounds having vapor pressures less than ~10^{-3} Pa undergo negligible evaporation during sampling.[19] When particles are collected on the vaporizer for TPTD analysis they are cooled in less than a microsecond to −50 °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^{-3} Pa. Compounds with higher vapor pressures are expected to be primarily in the gas phase prior to entering the TDPBMS.

Aerosol Analysis by Chemical Ionization Mass Spectrometry. Aerosol samples and standards were also analyzed off-line by chemical ionization mass spectrometry (CIMS). Samples were introduced into a VG Analytical 7070E double-focusing mass spectrometer by coating the sample onto a platinum wire and then desorbing inside the CI source. The source temperature was 200 °C and the CI reagent gas was NH_3. Particles from ~1 m^3 of environmental chamber air were collected on a PTFE filter and extracted in dichloromethane (DCM) for analysis. Carboxylic acid and peroxide standards were prepared in acetone.

Generation of Aerosol Standards for TDPBMS. As an aid in identifying aerosol components formed in environmental chamber reactions, organic aerosol standards were also analyzed by TDPBMS. Particles were generated by nebulizing a 0.1% (w/w) solution of the compound of interest in 1-propanol using a Collison atomizer with clean, dry air (RH < 0.1%, total hydrocarbons < 5 ppbv) as the carrier gas. The aerosol from the atomizer was passed through diffusion dryers containing activated charcoal to adsorb the solvent, leaving a polydisperse aerosol (mass median diameter ~0.2 μm) of the low-volatility solute, which was sampled directly into the TDPBMS. Glutaric acid, adipic acid, suberic acid, 3-hydroxy-3-methylglutaric acid, 2-oxoadipic acid, and succinyl peroxide were analyzed in real-time as pure compounds to obtain mass spectra, and by TPTD as a mixture with glutaric acid and adipic acid, which served as internal standards for measuring volatility.

Environmental Chamber Technique. Secondary organic aerosol was formed in a series of environmental chamber experiments from reactions of O_3 with cyclopentene, cyclohexene, cycloheptene, and cyclooctene in humid air. Aerosol was generated by reacting 1−3 ppmv of the cyclic alkene with 2−3 ppmv of O_3 in a 7000 L PTFE bag at room temperature (~23 °C). The chamber was filled with clean air (containing <5 ppbv hydrocarbons) from an Aadco pure air generator humidified to a relative humidity (RH) of ~30% by adding water vapor to the clean air stream. Approximately 1000 ppmv of cyclohexane was added to the chamber to scavenge >98% of the OH radicals formed in the alkene-O_3 reaction,[24] thereby eliminating products from OH reactions with the cyclic alkene. In one cyclohexene experiment, ~100 ppmv of formaldehyde was also added prior to the start of the reaction by evaporating a measured weight of paraformaldehyde into a clean air flow. This was done in order to investigate the possible formation of aerosol peroxyhemiacetals by reaction of hydroperoxides with aldehydes.[17,18] In other cyclohexene experiments, $\sim$1000 ppmv of 1-propanol or methanol (these also served as OH scavengers), or $\sim$100 ppmv of formaldehyde and $\sim$1000 ppmv of cyclohexane, were added to dry chamber air ($\sim$0.1% RH) prior to the start of the reaction. This allowed evaluation of the possible importance of products from reactions of water, other acidic compounds, or aldehydes with stabilized Criegee intermediates in the aerosol formation process.[17,18] The cyclic alkenes, cyclohexane, alcohols, and water were added by evaporating the heated liquids 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 $\sim$2% O_3/O_2. During all chemical additions, a fan was run to mix the chamber 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. Background contributions were subtracted from real-time mass spectra, but were only significant for a few low-mass ions from air, the OH scavenger, and solvent (for standards). Background mass spectra for reactions were measured prior to addition of O_3, and for standards were measured with no particles passing through the DMA. In some experiments aerosol size distributions were measured using a scanning electrical mobility spectrometer.[19,25] Particle concentrations were initially less than $\sim$10 cm^{-3} and then reached $\sim 10^4 - 10^5$ cm^{-3} a few minutes after addition of O_3. Within an hour, average particle diameters reached $\sim$0.2−0.4 μm. Aerosol wall losses are $\sim$15% hr^{-1} for these experiments.[26] Ozone concentrations were measured by drawing air through PTFE tubing into a Dasibi 1003-AH O_3 analyzer. After an experiment the chamber was evacuated, filled, and flushed until the next day or longer ($>$10 chamber volumes).

Results and Discussion

TDPBMS Analysis of Aerosol Products Formed from the Reaction of Cyclohexene and O_3 in Humid Air. The real-time TDPBMS mass spectra measured after 1 and 100 min of reaction of cyclohexene [C_6H_{10}] and O_3 at $\sim$30% RH are shown in Figure 1. The most important feature to note is that the spectrum is initially dominated at high mass by peaks at *m*/*z* (mass/charge ratio) 99 and 115 (Figure 1A), but over time the *m*/*z* 86 and 100 peaks increase and eventually become more intense than those at *m*/*z* 99 and 115 (Figure 1B). The aerosol composition clearly changes significantly over the course of the experiment.

In an effort to identify the components of the aerosol, particles were collected on a cold vaporizer after $\sim$2 h of reaction and analyzed by temperature-programmed thermal desorption (TPTD).[20] This technique separates compounds according to volatility, such that compounds with lower vapor pressures desorb at higher temperatures. The desorption profiles for *m*/*z* 86, 99, 100, and 115 are shown in Figure 2A, and indicate that the aerosol is composed of compounds with a wide range of vapor pressures. From the correlation between compound desorption temperature and vapor pressure at 25 °C shown in Figure 3, which was obtained by analysis of compounds of known vapor pressures under similar desorption conditions, we estimate that the 30−80 °C temperature range corresponds to vapor pressures of $\sim 10^{-4} - 10^{-7}$ Pa at 25 °C.

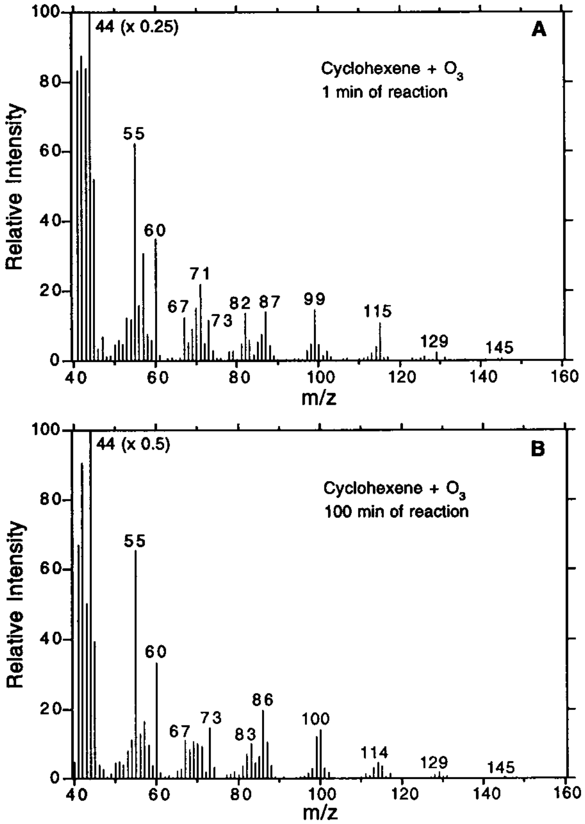


Figure 1. Real-time TDPBMS mass spectra of aerosol formed from reaction of cyclohexene with O_3 at $\sim$30% RH in the presence of an OH scavenger after (A) 1 min and (B) 100 min of reaction.

Figure 2B shows the full TPTD mass spectrum obtained by plotting the signal intensity at the maximum for all *m*/*z*'s that exhibit maxima within a 6 °C window centered at 45 °C, which is the maximum in the *m*/*z* 86 desorption profile. Because the signal intensities of all *m*/*z*'s associated with a particular compound should peak at the same temperature, this technique provides a means of extracting mass spectra of individual compounds from mixtures. The TPTD mass spectrum at 45 °C is an excellent match to that of glutaric acid (Figure 4A), thereby confirming the presence of this compound as a major aerosol component. Glutaric acid [$HO(O)C(CH_2)_3C(O)OH$] and adipic acid [$HO(O)C(CH_2)_4C(O)OH$] are dicarboxylic acids that have been consistently identified by GC-MS as major components in aerosol formed in the cyclohexene-O_3 reaction.[5,27] The TPTD mass spectrum extracted at 55 °C, which is the temperature at which *m*/*z* 100 reaches a maximum, is shown in Figure 2C. All of the major high-mass peaks in the adipic acid mass spectrum (Figure 4B), including *m*/*z* 82, 87, 100, and 128 are also prominent in the 55 °C spectrum, providing strong evidence for the presence of adipic acid. Some of the low mass peaks are absent, however, and a few additional peaks are present. The absence of the *m*/*z* 60 and 73 peaks is almost certainly because they are also present in glutaric acid, and tailing from the 45 °C peak of that compound obscures maxima at 55 °C in the *m*/*z* 60 and 73 desorption profiles. The intense peaks at *m*/*z* 57, 67, 70, 71, 98, 99, and 145 are probably associated with a compound (or compounds) with desorption behavior similar to adipic acid.

In the neighborhood of 75 °C, the desorption profile of *m*/*z* 115 exhibits a maximum. But many other desorption profiles only have shoulders (e.g., compare *m*/*z* 99 and 115 in Figure 2A), which would not be found by the program used to extract the mass spectra. Therefore, instead of plotting only the intensities of *m*/*z*'s that exhibit maxima in this region, which

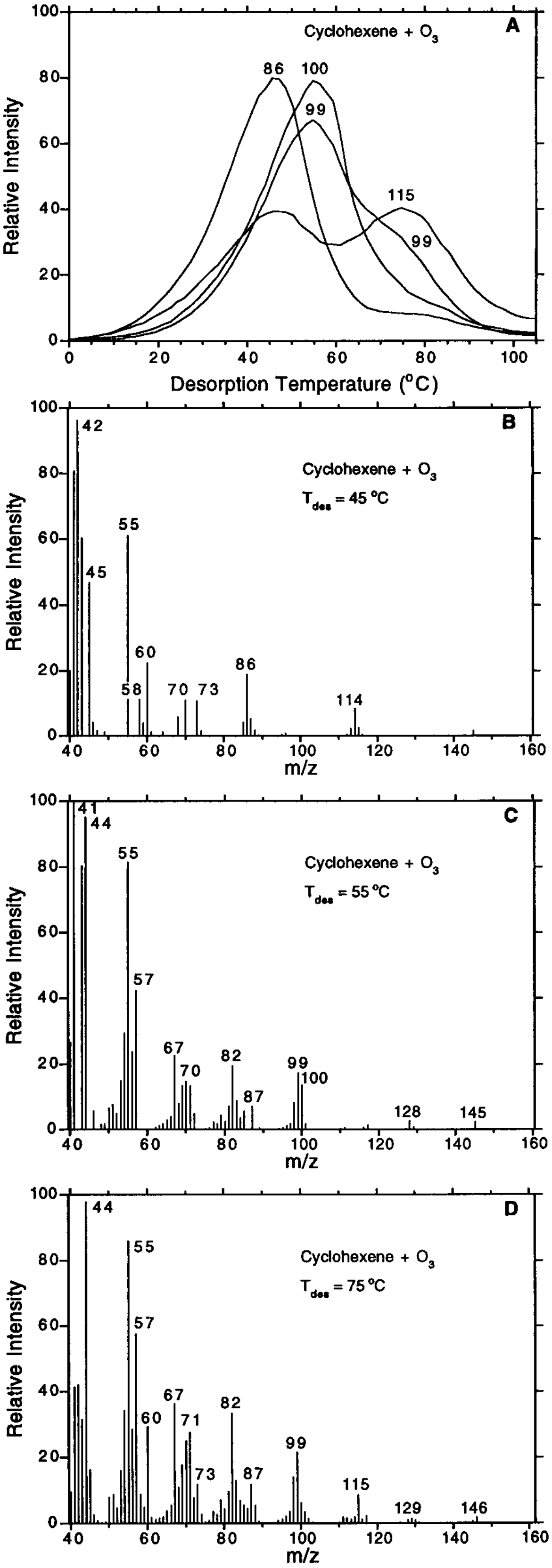


Figure 2. (A) TPTD desorption profiles of selected *m/z*'s and (B−D) TPTD mass spectra obtained at desorption temperatures of 45 °C, 55 °C, and 75 °C, respectively, for the aerosol products formed from reaction of cyclohexene with O_3 at ~30% RH in the presence of an OH scavenger. The curves have been scaled to similar intensities for easier comparison.

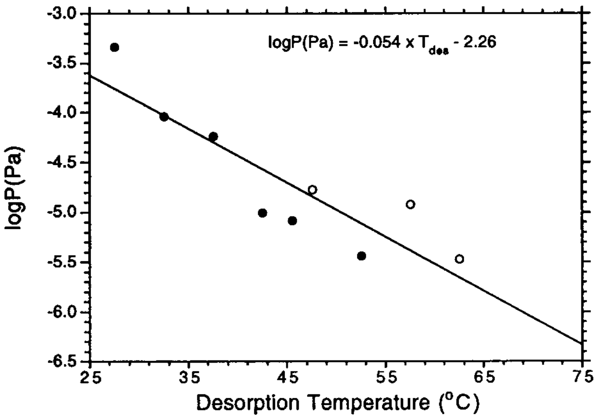


Figure 3. Correlation between compound vapor pressures at 25 °C and desorption temperatures measured by TPTD. Data are from previous TPTD measurements of C13−C18 monocarboxylic acid (filled circles) and C6−C8 dicarboxylic acid (open circles) vapor pressures.[23]

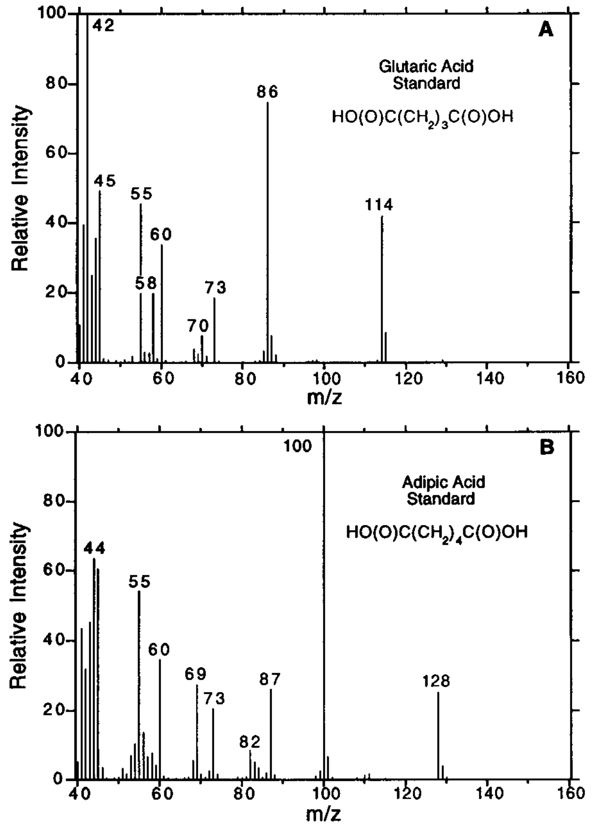


Figure 4. Real-time TDPBMS mass spectra of (A) glutaric acid and (B) adipic acid standards.

could eliminate some large peaks from the mass spectrum, in Figure 2D we plot the intensity of all *m/z*'s at 75 °C. This corresponds to a composite spectrum that is representative of the lowest volatility compounds. The spectrum has many peaks in common with the 55 °C spectrum (Figure 2C), especially if peaks associated with adipic acid are neglected. Even more noteworthy is the remarkable similarity to the real-time mass spectrum measured after 1 min of reaction (Figure 1A). The possible identity of the compounds responsible for these spectra are discussed below.

Particle Formation Dynamics in the Cyclohexene-O_3 Reaction. Nucleation is a complex process that depends on compound properties including partial pressure and equilibrium vapor pressure, surface tension, molecular weight, and molecular volume, and can involve one or more compounds.[7] It is therefore

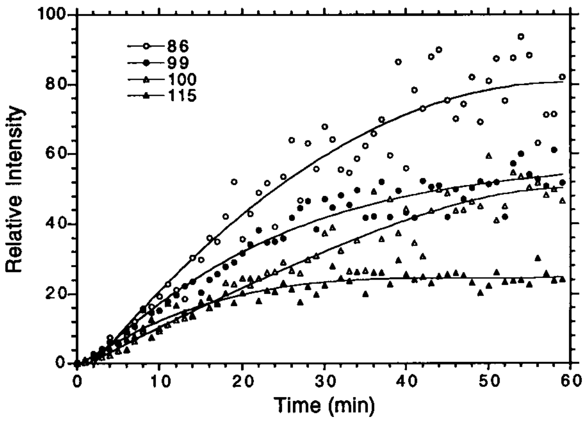


Figure 5. Time profiles of the real-time TDPBMS signal of *m*/*z* 86, 99, 100, and 115 ions from aerosol formed during the reaction of cyclohexene with O_3 at ~30% RH in the presence of an OH scavenger. The curves are polynomials fit to the data to aid the eye.

difficult to predict which species will nucleate in a particular system. Although we cannot measure the composition of freshly nucleated particles (a nanometer or so in size), the time-dependent mass spectra in Figure 1 and TPTD profiles in Figure 2A indicate that in this system particle formation is initiated by homogeneous nucleation of the lowest volatility compounds (as measured by thermal desorption temperatures). Following nucleation, growth occurs by condensation of the same species, with contributions from more volatile compounds such as adipic acid and glutaric acid increasing over time. This occurs because growth depends on the difference between condensation and evaporation rates, which in turn depends on the difference between compound partial pressures and equilibrium vapor pressures. This behavior is illustrated in greater detail in the time profiles of *m*/*z* 86, 99, 100, and 115 signal shown in Figure 5 for the first 60 min of the cyclohexene-O_3 reaction. Nucleation occurs within a minute of adding O_3, and over the next hour the signal increases due to condensational growth. During this period, the particle number concentration slowly decreases due to coagulation and wall loss, and beyond ~60 min all mass spectral peaks begin to decrease due to particle loss to the walls (data not shown). The profiles for the individual *m*/*z* reach plateaus in an order that depends on compound vapor pressure (or desorption temperature, T_{des}). The lowest volatility components level off first, as shown by *m*/*z* 115 ($T_{des} \approx 75$ °C), followed by *m*/*z* 99 ($T_{des} \approx 75$ °C and ~55 °C), adipic acid ($T_{des} \approx 55$ °C), and glutaric acid ($T_{des} \approx 45$ °C). From the rate constant for the reaction of cyclohexene with O_3 ($k = 8.1 \times 10^{-17}$ cm^{-3} molecule^{-1} s^{-1})[1,2] and the ~2−3 ppmv O_3 concentrations used in these experiments, we estimate that the cyclohexene-O_3 reaction is essentially complete in ~10−20 min. Changes in aerosol composition over times longer than this therefore reflect gas-particle partitioning of reaction products and, perhaps, heterogeneous chemical reactions, rather than gas-phase chemistry.

Identity of Low-Volatility Aerosol Compounds: Evidence Against Secondary Ozonides, Hydroperoxides, Peroxyhemiacetals, Diacyl Peroxyhemiacetals, Substituted Dicarboxylic Acids, and Dicarboxylic Acid Dimers. Although glutaric acid and adipic acid can be identified in the aerosol with confidence, it is more difficult to determine the identity of other low-volatility components because of the low resolution of the TPTD separation technique and the lack of mass spectral standards. This, however, is the most important question, because of the critical role that low-volatility compounds play in the nucleation and growth of atmospheric particles. Fortunately, the mass spectra, desorption temperatures, and nature of the reactants place relatively tight constraints on the possible aerosol products of the cyclohexene-O_3 reaction. The only means by which cyclohexene can be converted to compounds less volatile than the dicarboxylic acids is by extensive oxidation, or by oxidation followed by a reaction that combines two large molecules into one. In the following sections, we explore these possibilities.

Secondary Ozonides, Hydroperoxides, and Peroxyhemiacetals. In previous studies of aerosol formation from reaction of the linear alkene, 1-tetradecene [$CH_3(CH_2)_{11}CH{=}CH_2$],with O_3 in humid air we determined that the major aerosol products are secondary ozonides, hydroperoxides, and peroxyhemiacetals formed by a pathway involving stabilized Criegee intermediates (reactions 1−5).[17,18] Because reactions of cyclic alkenes with O_3 also generate stabilized Criegee intermediates, with a measured yield of ~3% for cyclohexene,[2] we first consider whether similar pathways might be important in aerosol formation for these compounds. The initial steps in the reaction are[1,2]

$$C_6H_{10} + O_3 \rightarrow [OHC(CH_2)_4CHOO]^* \qquad (6)$$

$$[OHC(CH_2)_4CHOO]^* \rightarrow \text{Products} \qquad (7)$$

$$[OHC(CH_2)_4CHOO]^* + M \rightarrow OHC(CH_2)_4CHOO + M \quad [M = N_2, O_2] \qquad (8)$$

Initially, O_3 adds to the double bond to form an excited primary ozonide, which rapidly decomposes to a bifunctional excited Criegee intermediate, $[OHC(CH_2)_4CHOO]^*$ (reaction 6). Excited Criegee intermediates undergo isomerization and decomposition reactions (reaction 7), or are stabilized by collisions with air (reaction 8). If aerosol formation in humid air involves reactions of stabilized Criegee intermediates with water vapor then the initial product is 6-hydroxy-6-hydroperoxyhexanal [$OHC(CH_2)_4CH(OH)OOH$]

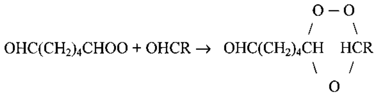
$$OHC(CH_2)_4CHOO + H_2O \rightarrow OHC(CH_2)_4CH(OH)OOH \qquad (9)$$

The hydroperoxide could then react with an aldehyde (e.g., monoaldehydes, dialdehydes, and oxoacids have been identified among the products of the cyclohexene reaction[5,27,28]) to form a low-volatility peroxyhemiacetal

$$OHC(CH_2)_4CH(OH)OOH + OHCR \rightarrow OHC(CH_2)_4CH(OH)OOCH(OH)R \qquad (10)$$

A variety of evidence suggests that reactions 9 and 10 are not important in aerosol formation. Independent, concurrent studies of this reaction using atmospheric pressure ionization mass spectrometry (API-MS) to identify gas-phase products found no evidence for 6-hydroxy-6-hydroperoxyhexanal,[29] even though the same technique has been used to identify hydroxyhydroperoxides formed from ozonolysis of 1-octene and 7-tetradecene.[30] It was concluded that 6-hydroxy-6-hydroperoxyhexanal rapidly decomposes to a dialdehyde by loss of H_2O_2 and, therefore, cannot lead to aerosol. The same appears to be true for the α-pinene[30] and β-pinene[14] reactions. As an additional check on this potential mechanism we carried out reactions with high concentrations (~1000 ppmv) of methanol [CH_3OH] and 1-propanol [$CH_3CH_2CH_2OH$] in dry air (RH < 0.1%). If stabilized Criegee intermediate reactions form aerosol, then under these conditions the alcohols should replace water in reaction 9, and the alkoxyhydroperoxides $OHC(CH_2)_4CH(OCH_3)OOH$ and $OHC(CH_2)_4CH(OCH_2CH_2CH_3)OOH$ and corresponding peroxyhemiacetals should replace the products of reactions 9 and 10.[17] Mass spectral peaks from the water reaction products should disappear, and, on the basis of the fragmentation patterns of similar compounds formed in the 1-tetradecene reaction,[17,18] major new peaks should appear at *m*/*z* 129 [$OHC(CH_2)_4CH(OCH_3)^+$] and 157 [$OHC(CH_2)_4CH(OCH_2CH_2CH_3)^+$]. There was, however, no significant change in the mass spectra.

Experiments were also performed to investigate the formation of secondary ozonides. These compounds were shown to be important in 1-tetradecene ozonolysis under dry conditions (reaction 3), and in their study of cyclohexene ozonolysis using API-MS, Aschmann et al.[29] observed a gas-phase C6 secondary ozonide formed by an intramolecular reaction of the Criegee intermediate. In the absence of added acidic species, stabilized Criegee intermediates could react with aldehydes according to the reaction



$$OHC(CH_2)_4CHOO + OHCR \rightarrow OHC(CH_2)_4\overset{O-O}{CH\ \ \ HCR}\!\underset{O}{} \qquad (11)$$

As shown previously,[18] the mass spectra of secondary ozonides exhibit distinctive mass spectra, typically including a molecular ion peak, which should be different from that observed in humid air. Furthermore, secondary ozonides formed by reaction with formaldehyde should be too volatile to form aerosol, thus dramatically reducing the mass spectral signal. Mass spectra obtained for reaction in dry air without added acidic species, with and without added formaldehyde, were again similar to that obtained in humid air.

These results indicate that aerosol formation from cyclohexene ozonolysis does not occur by reactions of stabilized Criegee intermediates, but through excited intermediates (reaction 7).

Diacyl Peroxyhemiacetals. It has recently been proposed that dicarboxylic acids are formed in reactions of substituted cyclic alkenes and O_3 through a mechanism involving excited Criegee intermediates.[13,14] A bifunctional oxoperoxyacid [OHCRC(O)-OOH] is formed initially, followed by an intramolecular reaction between the peroxyacid and aldehyde ends of the molecule to form a dicarboxylic acid

$$OHCRC(O)OOH \rightarrow HO(O)CRC(O)OH \qquad (12)$$

It is therefore important to consider whether the unidentified low-volatility compounds observed in the present study might be acyl peroxyhemiacetals formed by intermolecular reactions between peroxyacids and aldehydes, which are known to occur in solution[31]

$$OHCR_1C(O)OOH + OHCR_2 \rightarrow OHCR_1C(O)OOCH(OH)R_2 \qquad (13)$$

For example, the reaction could involve 1-oxoperoxypentanoic acid, $OHC(CH_2)_3C(O)OOH$, which has been identified among the gas-phase products of this reaction using API-MS.[29] The reaction would be similar to reaction 10, but involving a peroxyacid rather than a hydroxyhydroperoxide. To investigate this possibility, the cyclohexene-O_3 reaction was carried out at ~30% RH in the presence of a high concentration of formaldehyde (~100 ppmv). Previously, when a similar experiment was performed with 1-tetradecene, the C13 hydroxyhydroperoxide product reacted with formaldehyde, as in reaction 5. The product of the reaction with tridecanal [$CH_3(CH_2)_{11}CHO$], which formed in the absence of added formaldehyde, was no longer observed.[17,18] In the case of cyclohexene, however, no change was observed in the aerosol mass spectra or TPTD profiles when formaldehyde was added, indicating that no reaction occurred. Reaction 13 probably occurs only in the condensed phase, as appears to be the case for reaction 5.[17] It is therefore unlikely that acyl peroxyhemiacetals are the unidentified low-volatility products, although heterogeneous reactions could contribute to aerosol formation over longer time scales. As additional support for this conclusion, we note that Tuazon[32] recently used FTIR to monitor a mixture of ~1 ppmv each of peroxyacetic acid [$CH_3C(O)OOH$] and formaldehyde in a 5800 L reactor, with no evidence for any reaction over a 1 h period, and in their study of the cyclohexene-O_3 reaction using API-MS, Aschmann et al.[29] saw no evidence for reaction of $OHC(CH_2)_3C(O)OOH$ when acetaldehyde [CH_3CHO] or butanal [$CH_3(CH_2)_2CHO$] were added to the chamber.

Substituted Dicarboxylic Acids. Another class of compounds that should be less volatile than glutaric acid and adipic acid and, thus, desorb at higher temperatures, are hydroxyl- and carbonyl-substituted dicarboxylic acids. For example, hydroxyadipic acid and hydroxyglutaric acid have been identified by GC−MS analysis of cyclohexene-O_3 aerosol, although no oxodicarboxylic acids were reported.[5] Fortunately, we were able to obtain some of these compounds in order to investigate their properties. Mass spectra of 2-hydroxyglutaric acid [$HO(O)C(CH_2)_2CH(OH)C(O)OH$] and 2-oxoadipic acid [$HO(O)C(CH_2)_3C(O)C(O)OH$] are shown in Figure 6, and TPTD desorption profiles for glutaric acid, adipic acid, 3-hydroxy-3-methylglutaric acid [$HO(O)CCH_2C(OH)(CH_3)CH_2C(O)OH$], and 2-oxoadipic acid are shown in Figure 7. The desorption profiles for *m*/*z* 100 and 101 (Figure 7D), which are used to characterize adipic acid and succinyl peroxide, respectively, are slightly bimodal. This is because adipic acid has a small peak in its mass spectrum at *m*/*z* 101 (Figure 4B) and succinyl peroxide (Figure 6C) has a small peak in its mass spectrum at *m*/*z* 100. The desorption profile for 3-hydroxy-3-methylglutaric acid is also slightly bimodal (Figure 7B), but in this case *m*/*z* 103 is due solely to this compound. We have not seen this behavior previously, and are not certain of its cause. The additional small peak is not due to thermal decomposition, which has never been observed in TPTD analysis, even for labile peroxides. The similarity of the mass spectra (not shown) of the compounds desorbing at the two temperatures, and the chemical ionization mass spectrum shown below (Figure 8A), indicate that only 3-hydroxy-3-methylglutaric acid is present. One explanation is that some of the 3-hydroxy-3-methylglutaric acid formed a cyclic structure with reduced polarity and higher volatility. For this compound, hydrogen bonding between the hydroxyl and acid groups could occur through an energetically favored six-membered ring. This observation does not impact our interpretation of the aerosol profiles.

Because the desorption behavior of a particular compound can vary with sample size and matrix, absolute desorption temperatures of compounds analyzed in this study differ from one sample to another by approximately ±10 °C. When variations occur, the desorption temperatures of all compounds in a given sample will be shifted in the same direction, typically by similar amounts. To allow for a more direct comparison between desorption profiles of standards and chamber aerosol, glutaric acid and adipic acid were added to all the TPTD standards to serve as an internal reference. These same compounds are present naturally in the chamber aerosol. To simplify the discussion of the desorption profiles we have also shifted the temperature axes (by less than ± 10 °C) so that the *m*/*z* 86 profiles (from glutaric acid) peak at ~45 °C, which is typical for a small sample of pure glutaric acid minimally affected by sample size. In the following discussion, all desorption temperatures are therefore referenced to glutaric acid, which is assigned a desorption temperature of ~45 °C. It is important to stress that this adjustment in no way alters the fact that compounds that are observed to desorb at higher temperatures than glutaric acid and adipic acid, when contained in the same sample, must be less volatile than these dicarboxylic acids. The absolute difference in desorption temperatures can be used to estimate the corresponding differences in vapor pressures using Figure 3.

The mass spectra of 2-hydroxyglutaric acid (Figure 6A) and 2-oxoadipic acid (Figure 6B) show intense high-mass peaks at *m*/*z* 85 and 115, respectively. The probable fragmentation pathways are

$$\mathrm{HO(O)C(CH_2)_2CH(OH)C(O)OH^+} \rightarrow \mathrm{HO(O)CCH_2CHCH^+}\ (m/z\ 85) + \mathrm{H_2O} + \mathrm{C(O)OH} \quad (14)$$

$$\mathrm{HO(O)C(CH_2)_3C(O)C(O)OH^+} \rightarrow \mathrm{HO(O)C(CH_2)_3CO^+}\ (m/z\ 115) + \mathrm{C(O)OH} \quad (15)$$

By analogy, the mass spectrum of 2-hydroxyadipic acid [$\mathrm{HO(O)C(CH_2)_3CH(OH)C(O)OH}$] should have a large peak at *m*/*z* 99 [$\mathrm{HO(O)C(CH_2)_2CHCH^+}$], shifted by 14 mass units from that of 2-hydroxyglutaric acid. Formation of 2-hydroxyadipic acid and 2-oxoadipic acid might, therefore, provide an explanation for the *m*/*z* 99 and 115 peaks in the aerosol mass spectrum. The TPTD desorption profiles indicate that this is not the case, however, because 3-hydroxy-3-methylglutaric acid (an isomer of 2-hydroxyadipic acid) (Figure 7B) and 2-oxoadipic acid (Figure 7C) desorb at essentially the same temperature as adipic acid. By contrast, the lowest volatility compounds in the chamber aerosol desorb ~20 °C after adipic acid (Figure 2A).

As an additional test for substituted hydroxy- and oxo-dicarboxylic acids, chamber aerosol was collected on a filter and along with standards was analyzed off-line by chemical ionization mass spectrometry using NH_3 reagent gas. This method of ionization leads to less fragmentation than electron ionization. The CI mass spectra of 3-hydroxy-3-methylglutaric acid, 2-oxoadipic acid, succinyl peroxide, and chamber aerosol are shown in Figure 8. In the high-mass region, the mass spectra of 3-hydroxy-3-methylglutaric acid (Figure 8A), and adipic acid and glutaric acid (not shown), show major peaks at $m/z = 180$, 164, and 150, which correspond to $(M + \mathrm{NH_4})^+$, where M is the molecular weight. The mass spectrum of 2-oxoadipic acid is more complex, with significant peaks at *m*/*z* 161 $(M + \mathrm{H})^+$, 144, 132, and 113. The mass spectrum of the chamber aerosol shows major peaks at *m*/*z* 164 and 150 from adipic acid and glutaric acid, respectively, as well as lower mass peaks. No peaks are present corresponding to hydroxyglutaric acid (*m*/*z* 166), hydroxyadipic acid (*m*/*z* 180), oxoglutaric acid (*m*/*z* 147 and 130), or oxoadipic acid (*m*/*z* 161 and 144), providing further evidence that hydroxy- and oxo-dicarboxylic acids are not present in significant quantities.

We also consider the possible presence of peroxydicarboxylic acids such as 2-peroxyglutaric acid, $\mathrm{HO(O)C(CH_2)_2CH(OOH)C(O)OH}$, and 2-peroxyadipic acid, $\mathrm{HO(O)C(CH_2)_3CH(OOH)C(O)OH}$ in the aerosol. These compounds should be less volatile than hydroxydicarboxylic acids,[33] although by how much is uncertain. Furthermore, their presence might explain the hydroxyglutaric acid and hydroxyadipic acid identified by GC-MS in aerosol formed from this reaction.[5] Decomposition of the peroxides during derivatization might yield derivatives corresponding to hydroxy-substituted compounds. In this scenario, 2-peroxyglutaric acid would be the compound that desorbs close to adipic acid, and 2-peroxyadipic acid would be the compound that desorbs after adipic acid. We do not have mass spectra of these compounds, but 2-peroxyadipic acid fragmentation might be analogous to 2-hydroxyglutaric acid (Equation 14), forming *m*/*z* 115 by loss of $\mathrm{H_2O} + \mathrm{C(O)OH}$, and *m*/*z* 99 by loss of $\mathrm{H_2O_2} + \mathrm{C(O)OH}$. This agrees with the low-volatility compound mass spectrum (Figure 2D), but there is no reasonable pathway for forming *m*/*z* 129. Other problems with this assignment are that strong peaks would be expected at *m*/*z* 85 and 101 for 2-peroxyglutaric acid, which are not observed in Figure 2C, and there is no plausible pathway for forming *m*/*z* 99 for this compound. In addition, compounds larger than glutaric and adipic acid should be present in the aerosol CIMS

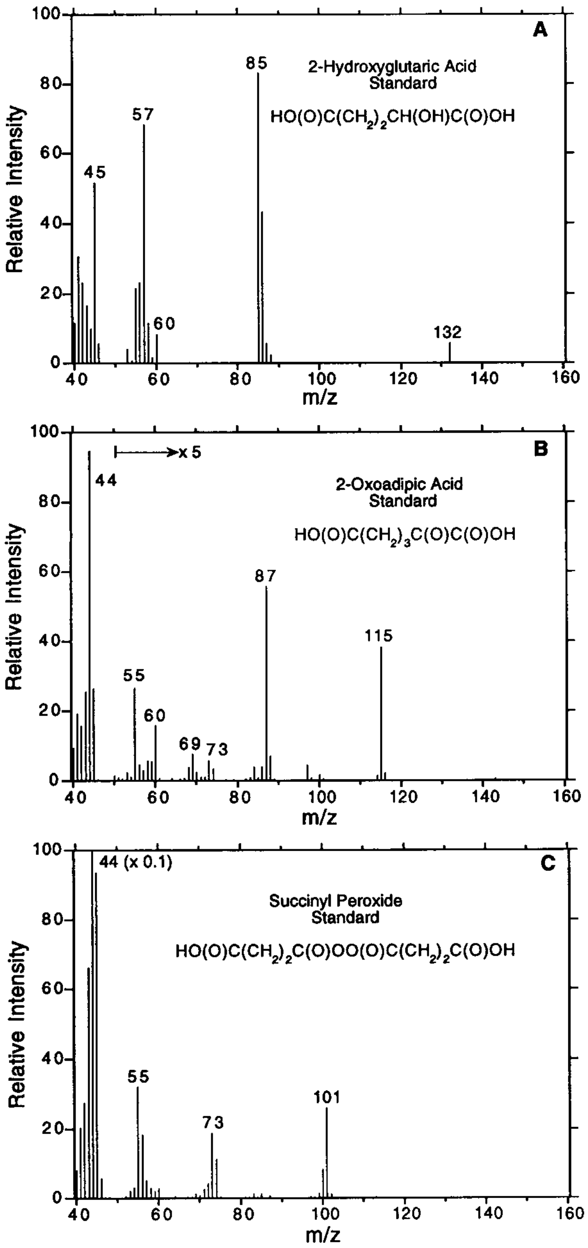


Figure 6. Mass spectra of (A) 2-hydroxyglutaric acid, (B) 2-oxoadipic acid, and (C) succinyl peroxide standards. The mass spectrum for 2-hydroxyglutaric acid is an electron ionization spectrum taken from the Wiley Library, and those for 2-oxoadipic acid, and succinyl peroxide were determined by real-time TDPBMS.

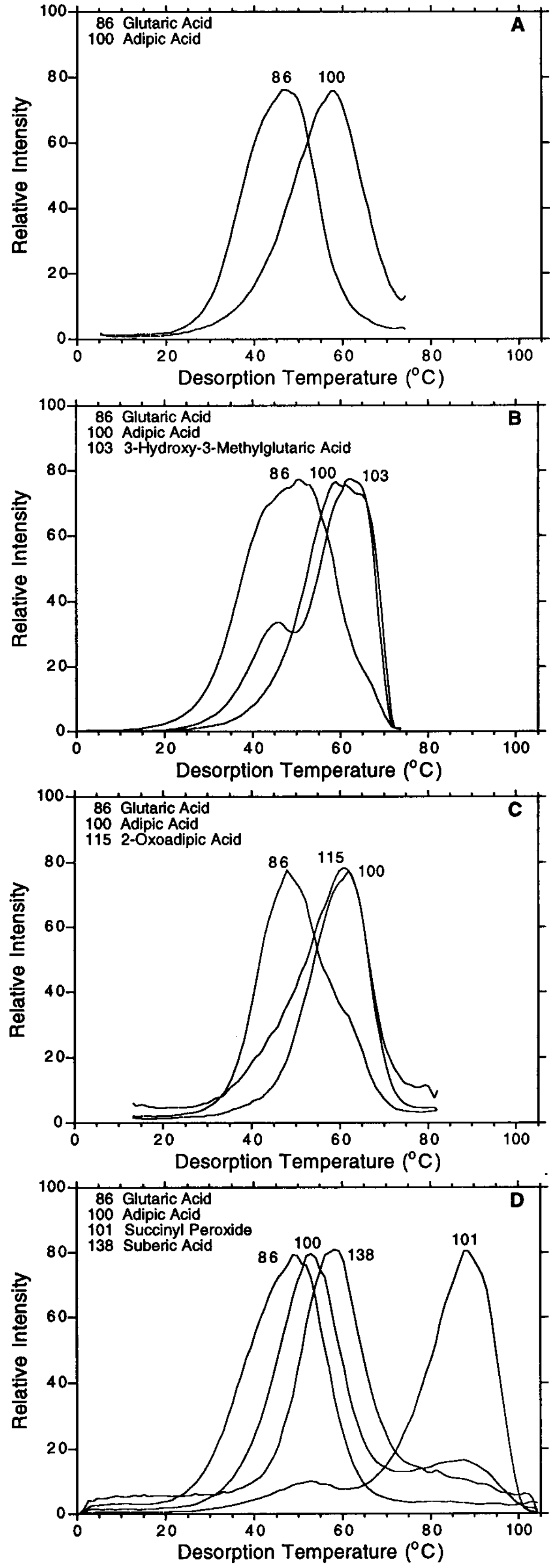


Figure 7. TPTD desorption profiles of selected *m*/*z*'s for mixed particle standards of (A) glutaric acid and adipic acid, (B) glutaric acid, adipic acid, and 3-hydroxy-3-methylglutaric acid, (C) glutaric acid, adipic acid, and 2-oxoadipic acid, and (D) glutaric acid, adipic acid, suberic acid, and succinyl peroxide. The curves have been scaled to similar intensities for easier comparison.

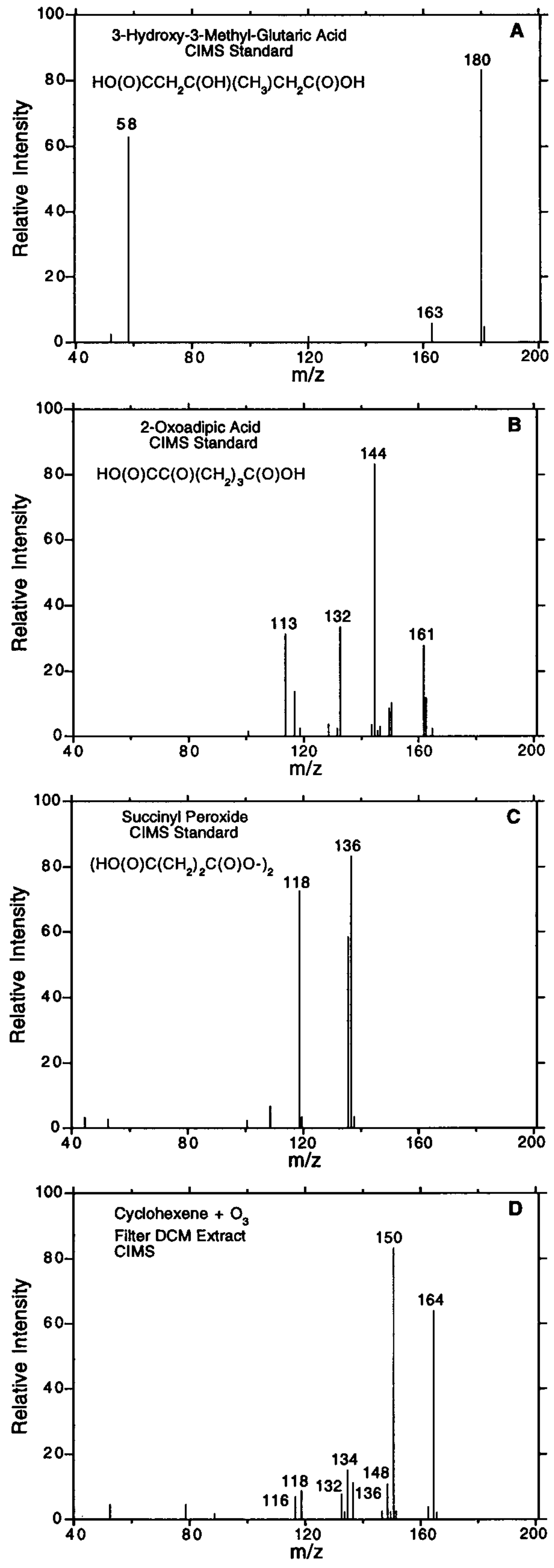


Figure 8. Ammonia chemical ionization mass spectra of standards of (A) 3-hydroxy-3-methylglutaric acid, (B) 2-oxoadipic acid, (C) succinyl peroxide, and (D) DCM extracted filter sample of aerosol formed from reaction of cyclohexene with O_3 at ~30% RH in the presence of an OH scavenger.

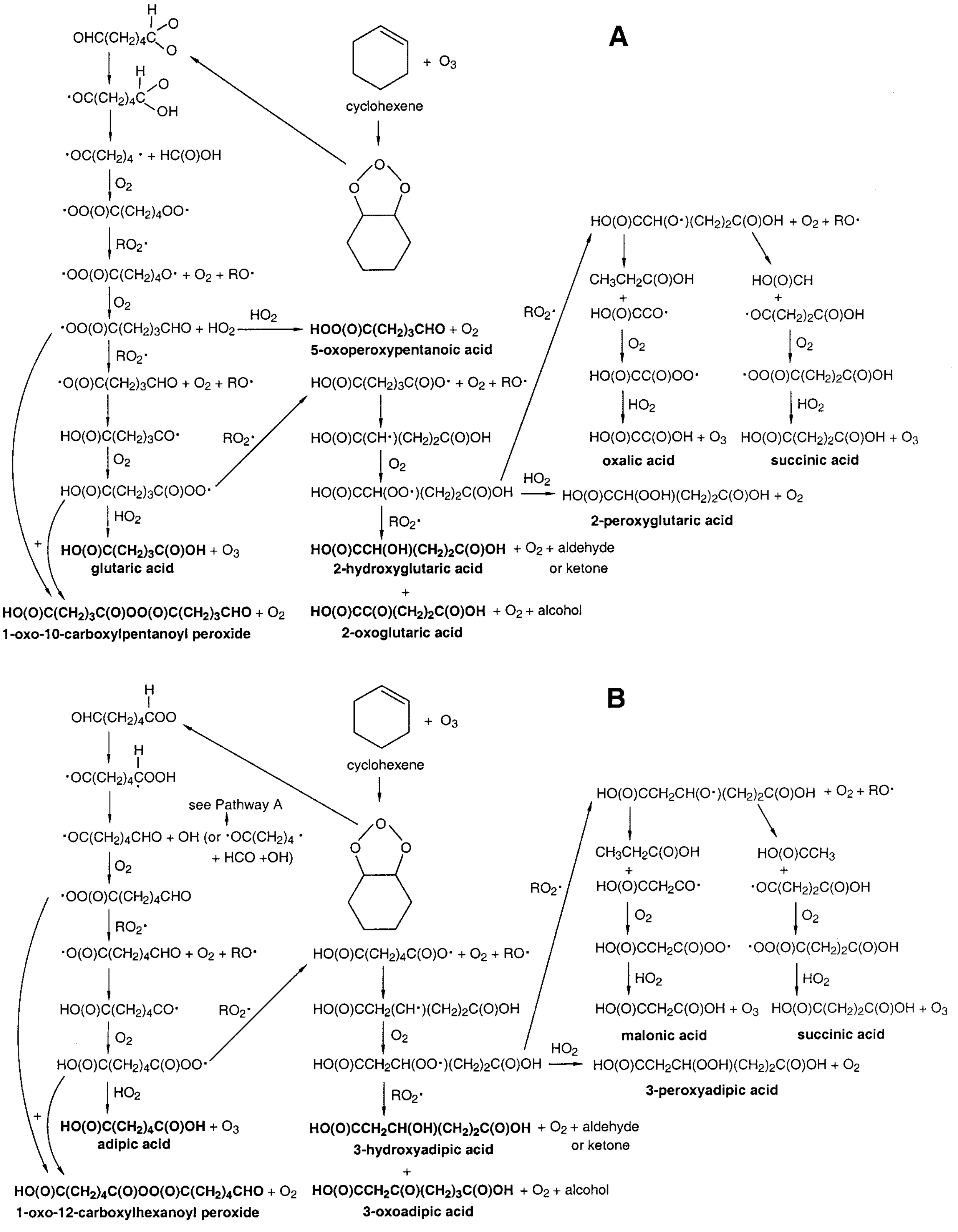


Figure 9. Proposed mechanism for forming (A) C10 diacyl peroxides and (B) C12 diacyl peroxides, and dicarboxylic acids from the reaction of cyclohexene with O_3 in the presence of an OH scavenger.

(Figure 8D), and it is quite likely (see the mechanism in Figure 9), that 2-peroxyadipic acid would not be a major isomer.

These results provide strong evidence that hydroxy- and oxo-dicarboxylic acids are not the unidentified low-volatility aerosol compounds, and the case for peroxydicarboxylic acids, although stronger, has serious weaknesses.

Dicarboxylic Acid Dimers. An alternative to forming species less volatile than dicarboxylic acids through chemical reactions is to create stable dimers through association of dicarboxylic acids. This mechanism has been proposed to explain the appearance of dimers of pinic acid and norpinic acid (C9 and C8 dicarboxylic acids) in aerosol formed from α-pinene ozonolysis, which was analyzed on-line by thermal desorption followed by API-MS.[34] If dimers of glutaric acid and adipic acid are somehow responsible for the peaks at *m*/*z* 99 and 115 observed here for the chamber aerosol, then these peaks should also be prominent in particles formed through homogeneous nucleation and condensation of glutaric acid and adipic acid vapors. When this experiment was performed by evaporating the diacids into a stream of clean air, the mass spectra looked like those in Figure 4, indicating that dicarboxylic acid dimers are not the unidentified low-volatility compounds formed in the cyclohexene-O_3 reaction.

Identity of Low-Volatility Aerosol Compounds: Evidence for Diacyl Peroxides and Proposed Mechanism of Formation. Because none of the classes of compounds described above provide a satisfactory explanation of the data, we propose that the unidentified low-volatility compounds are diacyl peroxides [$R_1C(O)OO(O)CR_2$]. A mechanism for their formation is presented below, which also explains the formation of dicarboxylic acids, and has similarities to reaction schemes recently proposed for the formation of pinic acid from ozonolysis of the cyclic monoterpenes α- and β-pinene.[13-15] We then show that the mass spectra and desorption temperatures are consistent with the expected reaction products.

The proposed mechanism for the formation of diacyl peroxides from the reaction of cyclohexene and O_3 in the absence of OH radicals is shown in Figure 9. The reaction begins with addition of O_3 to the double bond to form a primary ozonide, which decomposes to an excited Criegee intermediate, [$OHC(CH_2)_4CHOO$]*. In the scheme shown in Figure 9A, two O atoms in the Criegee intermediate are bonded separately to a terminal carbon, whereas in Figure 9B the bonding is C−O−O. In both cases, a terminal O atom then abstracts an H atom from the terminal carbonyl, which has the weakest hydrogen bond, and the resulting products decompose. In Figure 9A, decomposition leads to $OC(CH_2)_4$ + HC(O)OH (formic acid), and in Figure 9B to $OC(CH_2)_4CHO$ + OH (or $OC(CH_2)_4$ + HCO + OH). The latter pathways are the reason an OH scavenger is added to the reaction mixture.[1,2] Note that for simplicity of presentation, we have assumed that the excited Criegee intermediate in Figure 9A decomposes only by loss of formic acid, although it might also lose OH or HCO + OH, as shown in Figure 9B. Following decomposition, O_2, RO_2, and isomerization reactions lead to the acyl peroxy radicals $OO(O)C(CH_2)_3CHO$ and $OO(O)C(CH_2)_3C(O)OH$ (Figure 9A) and $OO(O)C(CH_2)_4CHO$ and $OO(O)C(CH_2)_4C(O)OH$ (Figure 9B), which have either a terminal carbonyl or carboxyl group, and either 5 (Figure 9A) or 6 (Figure 9B) carbon atoms. These radicals can then react with each other to form the diacyl peroxides $OHC(CH_2)_mC(O)OO(O)C(CH_2)_nCHO$ (dialdehydes), $OHC(CH_2)_mC(O)OO(O)C(CH_2)_nC(O)OH$ (oxoacids), and $HO(O)C(CH_2)_mC(O)OO(O)C(CH_2)_nC(O)OH$ (diacids), where m, $n = 3$ or 4. As examples, formation of the C10 and C12 oxoacids 1-oxo-10-carboxylpentanoyl peroxide [$OHC(CH_2)_3C(O)OOC(O)(CH_2)_3C(O)OH$] and 1-oxo-12-carboxylhexanoyl peroxide [$OHC(CH_2)_4C(O)OOC(O)(CH_2)_4C(O)OH$] are shown in Figures 9A and 9B, respectively. Furthermore, reactions of acyl peroxy radicals with HO_2 can lead to glutaric acid and adipic acid, and isomerization, decomposition, RO_2, O_2, and HO_2 reactions can lead to smaller dicarboxylic acids, and hydroxy-, oxo-, and peroxy-dicarboxylic acids. The substituted dicarboxylic acid isomers and smaller dicarboxylic acids shown here are those most likely to be formed because of the six-membered ring transition state that is preferred in the isomerization reaction.[1,2] Note that if species such as $HO(O)CCH(O\cdot)(CH_2)_2C(O)OH$ also split into HO(O)CCHO + $\cdot CH_2CH_2C(O)OH$, this pathway will lead to oxo-, hydroxy-, and unsubstituted monocarboxylic acids.

The TDPBMS mass spectrum of a diacyl peroxide dicarboxylic acid standard, succinyl peroxide [$HO(O)C(CH_2)_2C(O)OOC(O)(CH_2)_2C(O)OH$], is shown in Figure 6C. The major ions and probable fragmentation pathways are

$$HO(O)C(CH_2)_2C(O)OOC(O)(CH_2)_2C(O)OH^+ \rightarrow HO(O)C(CH_2)_2CO^+\ (m/z\ 101) + HO(O)C(CH_2)_2CO + O_2 \quad (16A)$$

$$\rightarrow HO(O)C(CH_2)_2^+\ (m/z\ 73) + HO(O)C(CH_2)_2CO + O_2 + CO \quad (16B)$$

There is also a large *m*/*z* 44 peak from CO_2^+. Ions such as $HO(O)C(CH_2)_2CO^+$ (*m*/*z* 101), with the structure RCO^+, are called acylium ions, and are known to be very stable and are generally observed in high abundance in mass spectra of compounds with carbonyl groups, such as ketones, esters, and acid anhydrides.[35] This was shown earlier for 2-oxoadipic acid (reaction 15). Acylium ions also often lose CO, as shown in reaction 16B.

The mass spectrum of a diacyl peroxide can be expected to be dominated by fragmentation patterns due to the two acyl peroxide radical subunits from which it is composed. The mass spectra of the 10 different diacyl peroxides that can be formed in the cyclohexene-O_3 reaction should therefore include some combination of peaks at *m*/*z* 99 and 71, 113 and 85, 115 and 87, and 129 and 101, generated by the pathways

$$RC(O)COOC(O)(CH_2)_3CHO^+ \rightarrow OHC(CH_2)_3CO^+\ (m/z\ 99) + RCO + O_2 \quad (17A)$$

$$\rightarrow OHC(CH_2)_3^+\ (m/z\ 71) + RCO + O_2 + CO \quad (17B)$$

$$RC(O)OOC(O)(CH_2)_4CHO^+ \rightarrow OHC(CH_2)_4CO^+\ (m/z\ 113) + RCO + O_2 \quad (18A)$$

$$\rightarrow OHC(CH_2)_4^+\ (m/z\ 85) + RCO + O_2 + CO \quad (18B)$$

$$RC(O)OOC(O)(CH_2)_3C(O)OH^+ \rightarrow HO(O)C(CH_2)_3CO^+\ (m/z\ 115) + RCO + O_2 \quad (19A)$$

$$\rightarrow HO(O)C(CH_2)_3^+\ (m/z\ 87) + RCO + O_2 + CO \quad (19B)$$

$$RC(O)OOC(O)(CH_2)_4C(O)OH^+ \rightarrow HO(O)C(CH_2)_4CO^+\ (m/z\ 129) + RCO + O_2 \quad (20A)$$

$$\rightarrow HO(O)C(CH_2)_4^+\ (m/z\ 101) + RCO + O_2 + CO \quad (20B)$$

Because a large number of compounds can be built from these same few subunits, a complex mixture can still have a relatively simple mass spectrum. The vapor pressures should decrease in the order dialdehydes > oxoacids > diacids, and with increasing carbon number.

The mass spectra of the unidentified low-volatility aerosol products formed in the cyclohexene-O_3 reaction are consistent with the major peaks expected from ionization of the proposed diacyl peroxide products, especially the C10 compounds. Large peaks are present at *m*/*z* 71, 87, 99, and 115, and there is a small local maximum at 129 (Figure 2D). There is also a very large peak at *m*/*z* 44, which appears to be characteristic of CO_2^+ ions from diacyl peroxides (Figure 6C). The intense peak at *m*/*z* 60 is characteristic of compounds containing carboxyl groups, but the fragmentation pathway by which it is formed is greatly enhanced in compounds that can form six-membered rings when the ionized carbonyl O atom abstracts an H atom from a neighboring CH_2 (i.e., a "McLafferty rearrangement").[35] This requires a $(CH_2)_3C(O)OH$ or larger chain, which is why the peak is small in succinyl peroxide (Figure 6c) and succinic acid $[HO(O)C(CH_2)_2C(O)OH]$,[36] but large in glutaric acid and larger diacids (Figure 4), and apparently in diacyl peroxides containing a $OC(CH_2)_3C(O)OH$ or $OC(CH_2)_4C(O)OH$ subunit. Plausible mechanisms can also be developed for the formation of other intense peaks, such as *m*/*z* 82, 73, and 67, but those will not be presented here. On the basis of the mass spectra and desorption profiles, we propose that the compound that desorbs along with adipic acid at 55 °C and produces large *m*/*z* 99 and 71 peaks is $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3CHO$. The compounds that desorb at 75 °C and produce peaks at *m*/*z* 71, 87, 99, 115, and 129 are probably $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$ and a small amount of $OHC(CH_2)_3C(O)OO(O)C(CH_2)_4C(O)OH$. There is no easily discerned contribution from compounds of the structure $OHC(CH_2)_4C(O)OO(O)CR$, which would produce *m*/*z* 113 ions.

The CI mass spectrum of the chamber aerosol filter sample is also reasonably consistent with the presence of compounds containing the $OHC(CH_2)_3C(O)O$ and $HO(O)C(CH_2)_3C(O)O$ moieties. Assuming that these compounds behave similarly to succinyl peroxide, peaks would be expected at *m*/*z* 134, 133, and 116 for compounds containing $OHC(CH_2)_3C(O)O$ and at *m*/*z* 150 (overlap with glutaric acid), 149, and 132 for compounds containing $HO(O)C(CH_2)_3C(O)O$. One should probably be cautious about interpreting peaks other than those of glutaric acid and adipic acid, however, because of the possibility of adsorption of gas-phase compounds such as oxomonocarboxylic acids and dialdehydes onto the filter. These types of compounds were not observed in TDPBMS analysis, but have been identified by GC-MS analysis of filter samples.[5] It is not clear at this point if the discrepancy in TDPBMS and GC-MS analyses is due to losses of volatile compounds during TDPBMS sampling, adsorption of gas-phase compounds to filters, or decomposition of peroxides during derivatization.

The diacyl peroxides are also consistent with the desorption temperatures that might be expected for these compounds. Here, we make a rough estimate for the desorption temperatures of $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3CHO$ and $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$ using a group additivity approach. We begin with glutaraldehyde $[OHC(CH_2)_3CHO]$, for which $T_{des} \approx 0$ °C (data not shown). We increase T_{des} by 10 °C by adding 3 CH_2 units, which is the difference between glutaric acid $[HO(O)C(CH_2)_3C(O)OH]$ and suberic acid $[HO(O)C(CH_2)_6C(O)OH]$ (Figure 7D), to make $OHC(CH_2)_6CHO$. We then increase T_{des} by another 35 °C by adding a $C(O)OOC(O)$ group in the center of the molecule, which is the difference between adipic acid $[HO(O)C(CH_2)_4C(O)OH]$ and succinyl peroxide $[HO(O)C(CH_2)_2C(O)OOC(O)(CH_2)_2C(O)OH]$ (Figure 7D), to make $OHC(CH_2)_3C(O)OOC(O)(CH_2)_3CHO$. This gives $T_{des} \approx 45$ °C, which is close to $T_{des} \approx 55$ °C of the first *m*/*z* 99 peak, which we assigned to this compound. We then convert this dialdehyde to the diacid, $HO(O)C(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$, and increase T_{des} to $\sim$100 °C by adding 45 °C, which is the difference between glutaraldehyde and glutaric acid. This value is $\sim$10 °C higher than T_{des} of succinyl peroxide, which is expected since the latter has 2 fewer CH_2 units. Assuming that the C10 oxoacid $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$ desorbs midway between the C10 dialdehyde and C10 diacid we obtain $T_{des} \approx 75$ °C, which is close to the location of the second *m*/*z* 99 and 115 peaks that we assigned to this compound.

Because $OHC(CH_2)_3C(O)OOC(O)(CH_2)_3CHO$ desorbs at the same temperature as adipic acid (55 °C), it should have a similar vapor pressure, which has been measured to be $\sim 1 \times 10^{-5}$ Pa at 25 °C.[23,37] The oxoacid $OHC(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$ desorbs $\sim$20 °C after adipic acid (75 °C), which from Figure 3 corresponds to approximately a factor of 10 decrease in vapor pressure. The vapor pressure of this compound is therefore probably $\sim 1 \times 10^{-6}$ Pa. The C10 diacid, $HO(O)C(CH_2)_3C(O)OO(O)C(CH_2)_3C(O)OH$, although not observed here, should have a vapor pressure of $\sim 10^{-7}-10^{-8}$ Pa, on the basis of the $T_{des} \approx 100$ °C estimated above.

The proposed mechanism for forming diacyl peroxides is consistent in most respects with other studies. The formation of an excited Criegee intermediate is well established, but abstraction of an H atom is usually assumed to occur from the adjacent C atom. Our hypothesis that an H atom is abstracted from the terminal carbonyl is the same as that used by Hatekeyama et al.[27,28] to explain the results of FTIR analyses of the gas-phase products of the reaction of cyclopentene and $^{18}O_3$. They observed that all formic acid and most of the CO_2 and CO formed were completely labeled with the ^{18}O isotope, which indicated they came predominantly from the decomposition of the Criegee intermediate (note that HCO formed in Figure 9B would rapidly be converted to CO by reaction with O_2). In the scheme that leads to C5 diacyl peroxides (Figure 9A), the formation of a key acyl peroxy radical, $OHC(CH_2)_3C(O)OO$, is supported by evidence from an API-MS study that identified 1-oxo-peroxypentanoic acid, $OHC(CH_2)_3C(O)OOH$, as a reaction product.[29] This species could be formed by the reaction of $OHC(CH_2)_3C(O)OO$ and HO_2, as shown in Figure 9A. A similar acyl peroxy radical intermediate has been proposed in mechanisms of dicarboxylic acid formation in a recent theoretical study[15] and in experimental studies[13,14] of the reactions of substituted cyclic alkenes (e.g., α-pinene and β-pinene) with O_3. The proposed mechanisms differ in that in one,[15] dicarboxylic acids form by the reactions

$$\mathrm{OHCRC(O)OO + RO_2 \rightarrow OHCRC(O)O + RO + O_2} \tag{21}$$

$$\mathrm{OHCRC(O)O \rightarrow OCRC(O)OH} \tag{22A}$$

$$\mathrm{\rightarrow OHCR + CO_2} \tag{22B}$$

$$\mathrm{OCRC(O)OH + O_2 + RO_2 \text{ or } HO_2 \rightarrow HO(O)CRC(O)OH} \tag{23}$$

and in the other,[13,14] by the reaction

$$\mathrm{OHCRC(O)OO + HO_2 \rightarrow OHCRC(O)OOH} \tag{24}$$

followed by reaction 12. It is important to note that in the first scheme electronic structure calculations indicate that abstraction of the aldehydic hydrogen in reaction 22A is sufficiently rapid to compete with decomposition of the acyl oxy radical by reaction 22B.

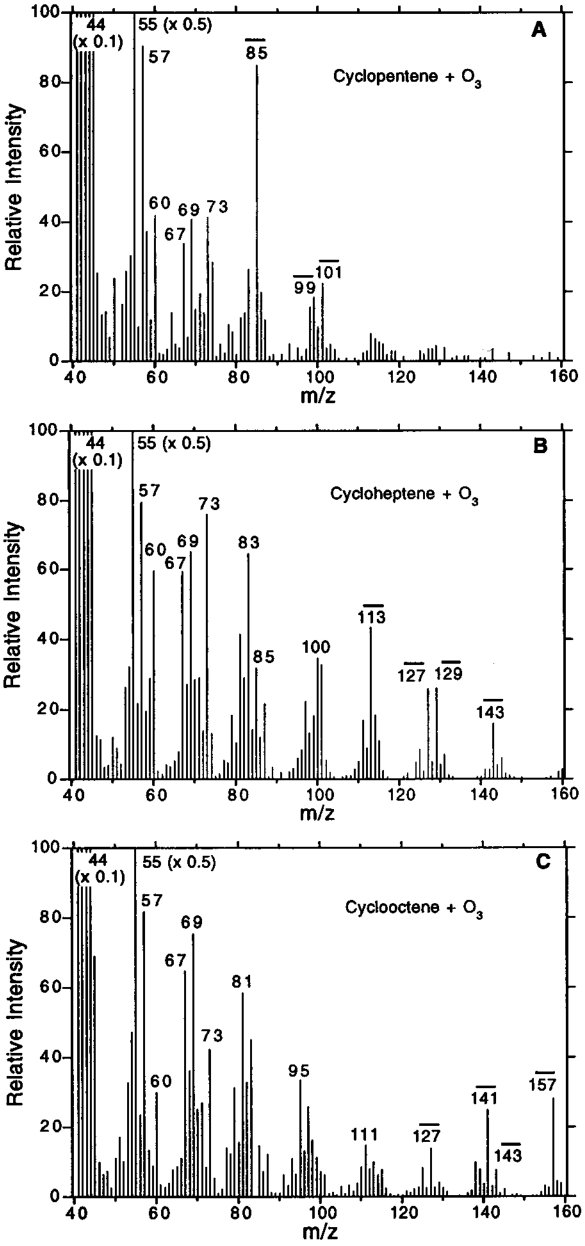


Figure 10. Real-time TDPBMS mass spectra of aerosol formed from reaction of (A) cyclopentene, (B) cycloheptene, and (C) cyclooctene with O_3 at ~30% RH in the presence of an OH scavenger. The lined peaks correspond to the major high-mass ion fragments expected to be observed if diacyl peroxides are present in the aerosol.

Our mechanism follows more closely the first of these with respect to reactions that lead to dicarboxylic acids. But the proposed association reaction between acyl peroxy radicals to form diacyl peroxides has not been shown to occur. This reaction was proposed as a radical chain termination step in the gas-phase auto-oxidation of acetaldehyde, on the basis of kinetic studies and the identification by low-temperature GC of diacyl peroxides among the reaction products.[38] Later studies using in situ spectroscopic techniques found no evidence for diacyl peroxides, although peroxy acetic acid was present (ref 39 and references therein). There is also inconclusive evidence that peroxy radicals undergo association reactions in the gas phase.[39] It may be that the smaller diacyl peroxides are unstable, whereas the larger diacyl peroxides, which might form due to their longer excited state lifetimes and greater chance of collisional stabilization, would be difficult to detect in the gas phase by FTIR or API-MS if they partition into particles. It is also likely that the yields of these compounds will be small, and so may have been missed. The molar yield of total aerosol for the cyclohexene + O_3 reaction is only ~10%.[5]

TDPBMS Analysis of Aerosol Products Formed from the Reactions of Cyclopentene, Cycloheptene, and Cyclooctene with O_3 in Humid Air. As an additional test of our hypothesis that diacyl peroxides are formed in the reaction of cyclohexene and O_3, we carried out a series of similar experiments with cyclohexene homologues, including cyclopentene [C_5H_8], cycloheptene [C_7H_{12}], and cyclooctene [C_8H_{14}]. On the basis of the mechanism proposed above, the diacyl peroxide products should be $OHC(CH_2)_mC(O)OO(O)C(CH_2)_nCHO$, $OHC(CH_2)_mC(O)OO(O)C(CH_2)_nC(O)OH$, and $HO(O)C(CH_2)_mC(O)OO(O)C(CH_2)_nC(O)OH$, where m and n are equal to either 2 or 3 for cyclopentene, 4 or 5 for cycloheptene, and 5 or 6 for cyclooctene. The major high-mass ions in the mass spectra should then be m/z 85, 99, 101, and 115 for cyclopentene, 113, 127, 129, and 143 for cycloheptene, and 127, 141, 143, and 157 for cyclooctene, formed according to reactions 17A, 18A, 19A, and 20A. The real-time mass spectra for the chamber reactions are shown in Figure 10. In all cases the major high-mass peaks in the mass spectra correspond to expected diacyl peroxide fragments, as labeled in the figure. Most of the other intense peaks can be explained as fragments from the diacyl peroxides (e.g., formed by loss of CO, H_2O, or CH_2 units from the major ions) or from the C5−C8 dicarboxylic acids. The TPTD desorption profiles are not shown, but reveal that the aerosol contains dicarboxylic acids and lower volatility compounds that are associated with the labeled high-mass ion fragments.

Conclusions

In previous studies of aerosol formation from reactions of O_3 with cyclohexene and homologous compounds, the least volatile compounds identified were dicarboxylic acids. Although dicarboxylic acids are observed here, the thermal desorption behavior of the aerosol indicates that less volatile compounds are also present. The TDPBMS mass spectra and desorption behavior of the aerosol and standard compounds, when combined with chemical probe experiments and off-line CIMS analyses, indicate that the unidentified low-volatility compounds are not secondary ozonides, hydroperoxides, peroxyhemiacetals, acyl peroxyhemiacetals, substituted dicarboxylic acids, or dicarboxylic acid dimers. On the basis of the evidence presented we propose that these compounds are diacyl peroxides, and propose a mechanism by which they could be formed. The key step in the reaction scheme involves association of acyl peroxy radicals to form diacyl peroxides, a reaction which is not known to occur in the gas phase. Our thought is that the molecules formed in these reactions are much larger than those studied previously, and can live long enough to be collisionally stabilized. Because the proposed mechanism for diacyl peroxide formation only involves gas-phase species, these compounds could play a role in particle nucleation.

These results may be relevant to atmospheric aerosol chemistry in light of a recent modeling study which indicates that the vapor pressures of compounds identified to date in laboratory reactions of monoterpenes, including dicarboxylic acids, are 2−3 orders of magnitude too high to explain the rates at which freshly nucleated atmospheric particles grow to the size of cloud condensation nuclei (~60−80 nm).[40] Identifying these low-volatility species is crucial to understanding the potential role of organic compounds in atmospheric aerosol chemistry and cloud formation, and their effect on global climate. In addition, the realm of the proposed reactions might not be limited to cyclic alkenes. For example, studies of the photochemical oxidation of toluene indicate that secondary reactions with O_3 contribute significantly to aerosol formation.[41] It may be that the unsaturated compounds formed by reactions of aromatic compounds with OH radicals[8] react with O_3 to form compounds similar to those observed here. This study may therefore provide insights that apply more generally to the mechanisms of aerosol formation from hydrocarbon oxidation. Mass spectra obtained in preliminary studies of reactions of O_3 with substituted cyclic alkenes, such as α-pinene, indicate the possible presence of some of the same types of aerosol compounds as proposed here for reactions of simple cyclic alkenes. More definitive identification of these products is needed, however, and will be addressed using wet chemical, separation, and spectroscopic techniques currently being developed. Furthermore, although the results presented here are clearly relevant to understanding laboratory studies of atmospheric chemistry, experiments need to be performed at lower reactant concentrations to evaluate the importance of these reactions under ambient conditions.

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