

Products of the Gas-Phase Reaction of O₃ with Cyclohexene

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Received: September 24, 2002; In Final Form: January 15, 2003

Products of the gas-phase reactions of O₃ with cyclohexene and cyclohexene-*d*₁₀ were investigated in the presence of OH radical scavengers by gas chromatography with flame ionization detection, combined gas chromatography–mass spectrometry, in situ Fourier transform infrared spectroscopy, and in situ atmospheric pressure ionization mass spectrometry (API-MS). Cyclohexane and cyclohexane-*d*₁₂ were used as OH radical scavengers in the experiments using API-MS analyses to allow products formed from the O₃ reactions with cyclohexene and cyclohexene-*d*₁₀ to be differentiated from those from the reactions of OH radicals with cyclohexane and cyclohexane-*d*₁₂. The gas-phase products observed from the reaction of O₃ with cyclohexene in the presence of an OH radical scavenger were pentanal (23.6 ± 1.8%); OH radicals (54 ± 8%); formic acid (3.5% initial yield); glutaraldehyde [HC(O)CH₂CH₂CH₂CHO]; adipaldehyde [HC(O)CH₂CH₂CH₂CH₂CHO], a C₆H₁₀O₃ product attributed to the secondary ozonide; a C₅H₇O₂(OOH) product, a molecular weight 130 hydroxydicarbonyl; and a molecular weight 116 carbonyl compound. Yields of pentanal-*d*₁₀, OD radicals, and DC(O)OH from the reaction of O₃ with cyclohexene-*d*₁₀, of 16.4 ± 1.4%, 50 ± 7%, and 1.6% (initial), respectively, were obtained. Our data indicate that reactions of the Criegee intermediate to form pentanal (plus CO₂) and an OH radical plus organic radical coproduct account for 78 ± 9% of the reaction pathways, with the organic radical coproduct reacting to form (in part) glutaraldehyde. Adipaldehyde can be formed from reaction of the thermalized Criegee intermediate (presumably the *anti*-intermediate) with water vapor. OH (or OD) radical formation yields were also measured from the reactions of O₃ with propene (40 ± 6%), propene-*d*₆ (27 ± 4%) α -pinene (86 ± 13%), and 2,3-dimethyl-2-butene (107 ± 16%).

Introduction

Alkenes are emitted into the atmosphere from anthropogenic and biogenic sources.¹ In the troposphere, alkenes react with OH radicals, NO₃ radicals, and O₃,^{1–3} with the O₃ reactions often being an important transformation process during both daytime and nighttime.^{1,3} The reactions of O₃ with alkenes lead to the production of OH radicals, often in high yield,^{2,3} and these reactions also lead to the formation of secondary organic aerosol.^{4–8} While the initial steps involved in the reactions of O₃ with alkenes are understood,^{1–3} there are many details of the complete reaction schemes which require investigation, and these include the identity of the reaction products which initiate formation of secondary organic aerosol, and the reactions of the stabilized Criegee intermediates. For example, it has been reported that the reaction of O₃ with cyclohexene (a symmetrical cycloalkene which can serve as a model compound for several monoterpenes emitted from vegetation) forms C₅- and C₆-dicarboxylic acids which nucleate and/or partition into seed particles and are important components of secondary organic aerosol.^{5,7,8} However, the routes leading to formation of these dicarboxylic acids are at present speculative.

To complement a recent study by Ziemann⁸ of the aerosol-phase products formed from the reaction of O₃ with cyclohexene, in this work we have used gas chromatography with flame ionization detection (GC-FID), combined gas chromatography–

mass spectrometry (GC-MS), in situ Fourier transform infrared spectroscopy (FT-IR), and in situ atmospheric pressure ionization tandem mass spectrometry (API-MS) to investigate the gas-phase products formed from the reactions of cyclohexene and cyclohexene-*d*₁₀ in the presence of OH radical scavengers. The use of cyclohexane and cyclohexane-*d*₁₂ as OH radical scavengers in the experiments with API-MS analyses allowed the products arising from the reactions of O₃ with cyclohexene to be differentiated from those formed from the OH radical reaction with cyclohexane, and investigation of the cyclohexene-*d*₁₀ reaction further aided in the elucidation of products using API-MS. As part of this work, the use of 2,3-butanediol as a radical scavenger to determine OH radical formation from the reactions of O₃ with cyclohexene and cyclohexene-*d*₁₀ was validated.

Experimental Section

Experiments were carried out at atmospheric pressure of air and at 296–298 K in a 5800 L evacuable, Teflon-coated chamber equipped with a multiple-reflection optical system interfaced to a Nicolet 7199 FT-IR spectrometer, in a ~8000 L Teflon chamber with off-line analyses by GC-FID, and in a ~7000 L Teflon chamber interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS). The experiments with GC-FID, GC-MS and API-MS analyses were carried out at ~5% relative humidity (~3.4 × 10¹⁶ molecule cm⁻³ of water).

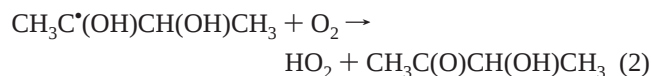
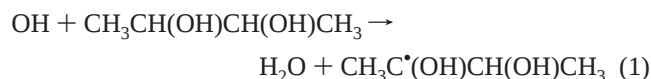
GC-FID Analyses. Two series of O₃/cyclohexene (or cyclohexene-*d*₁₀)/scavenger/air reactions were carried out, with analysis by gas chromatography with flame ionization detection (GC-FID) and with the scavenger being present to (a) react with

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the OH radicals formed in the reactions of O₃ with cyclohexene^{9,10} or cyclohexene-*d*₁₀ and (b) to enable the OH radical formation yields from the O₃ reactions to be derived from measurements of a product(s) of the OH radical reaction with the scavenger compound.^{9,11} Previously cyclohexane was employed as a radical scavenger,⁹ but because of uncertainties in the yields of the products measured to quantify the amount of OH radical formation, 2-butanol has more recently been employed with measurements of the amounts of 2-butanone formed.^{11,12} However, on the DB-1701 column used to separate 2-butanone from a large excess of 2-butanol, cyclohexene and 2-butanone coeluted. Therefore, a number of other diol and hydroxycarbonyl scavengers were investigated, with the goal being to measure the amounts of hydroxycarbonyl or dicarbonyl products formed, respectively. For example, when 2,3-butanediol was used as an OH radical scavenger the product monitored was 3-hydroxy-2-butanone.¹³



The OH radical scavengers investigated were 1,2-, 1,3-, and 2,3-butanediol, for which the rate constants for their reactions with OH radicals and the formation yields of the corresponding hydroxyketone have been measured.¹³ Another potential scavenger, 4-hydroxy-3-hexanone, had as an impurity ~0.7% of 3,4-hexanedione, its OH radical reaction product. Hence in the presence of $\sim 1.5 \times 10^{15}$ molecule cm⁻³ of 4-hydroxy-3-hexanone, the level required for efficient scavenging of OH radicals, formation of 3,4-hexanedione during the O₃ reactions would have been relatively small compared to its initial concentration. As in our previous study using 2-butanol as the OH radical scavenger,¹¹ in preliminary experiments we investigated formation of the hydroxycarbonyls from the diols in the presence of O₃, with the diol and O₃ concentrations being $\sim 1.7 \times 10^{15}$ molecule cm⁻³ and $(4-5) \times 10^{12}$ molecule cm⁻³, respectively. On the basis of the concentrations of the hydroxycarbonyls initially present and the amounts formed in the presence of O₃, we decided to use 2,3-butanediol as the OH radical scavenger, with formation of 3-hydroxy-2-butanone in $89 \pm 9\%$ yield from the OH radical-initiated reaction.¹³ To test the use of 2,3-butanediol as a radical scavenger to measure OH radical yields, OH radical formation yields from the reactions of O₃ with propene (and propene-*d*₆), α -pinene, and 2,3-dimethyl-2-butene were also measured.

The initial reactant concentrations (molecule cm⁻³ units) were cyclohexene or cyclohexene-*d*₁₀, $(2.20-2.47) \times 10^{13}$; 2,3-butanediol, 1.7×10^{15} ; or cyclohexane (used as the OH radical scavenger in certain of the experiments to measure the yields of pentanal or pentanal-*d*₁₀), 4.9×10^{15} ; and four additions of 50 cm³ volume O₃/O₂ aliquots were made to the chamber during an experiment, with each O₃/O₂ addition corresponding to an initial concentration of O₃ in the chamber of $\sim 5 \times 10^{12}$ molecule cm⁻³. The water vapor concentration was $\sim 3.4 \times 10^{16}$ molecule cm⁻³ (~5% relative humidity). The concentrations of cyclohexene and cyclohexene-*d*₁₀ and of selected products were measured during the experiments by GC-FID. For the analyses of cyclohexene and cyclohexene-*d*₁₀, gas samples were collected from the chamber into 100 cm³ volume all-glass gastight syringes and transferred via a 1 cm³ gas sampling loop onto a 30 m DB-5 megabore column held at -25 °C and then

temperature programmed at 8 °C min⁻¹ to 200 °C. For the analysis of pentanal (or pentanal-*d*₁₀) and 3-hydroxy-2-butanone, 100 cm³ volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~250 °C onto a 30 m DB-1701 megabore column held at -40 °C and then temperature programmed to 200 °C at 8 °C min⁻¹. GC-FID response factors were determined by introducing measured amounts of the chemicals into the chamber and conducting several replicate GC-FID analyses.

GC-MS Analyses. To identify carbonyls as their oxime derivatives, experiments were also carried out in which a 65 μm PDMS/DVB Solid-Phase Micro Extraction (SPME) fiber¹⁴ coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFB-HA) hydrochloride¹⁵ was exposed to the chamber reaction products and then analyzed by combined gas chromatography-mass spectrometry (GC-MS) with thermal desorption onto a 30 m DB-1701 fused silica capillary column in a Varian 2000 GC/MS/MS with analysis by isobutane chemical ionization. Carbonyl-containing products were examined from cyclohexene and cyclohexene-*d*₁₀ reactions in which cyclohexane was used as the OH radical scavenger. Standards of pentanal and glutaraldehyde were analyzed to confirm the retention times and mass spectra of their oxime derivatives.

API-MS Analyses. In these experiments, the chamber contents were sampled through a 25 mm diameter x 75 cm length Pyrex tube at ~ 20 L min⁻¹ directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision activated dissociation (CAD)] modes has been described previously.¹⁶ Use of the MS/MS mode with CAD allows the "product ion" or "precursor ion" spectrum of a given ion peak observed in the MS scanning mode to be obtained.¹⁶

The majority of the data obtained used the positive ion mode, in which protonated water hydrates (H₃O⁺ (H₂O)_{*n*}) generated by the corona discharge in the chamber diluent air were responsible for the protonation of analytes.^{16,17} Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. In these experiments the API-MS instrument was operated under conditions that favored the formation of dimer ions in the ion source region.¹⁶ Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain gas"), and as a result of the declustering action of the curtain gas on the hydrated ions, the ions that are mass analyzed are mainly protonated molecular ions ([M + H]⁺) and their protonated homo- and hetero-dimers.¹⁶

Experiments were carried out with cyclohexene + cyclohexane, cyclohexene-*d*₁₀ + cyclohexane, cyclohexene + cyclohexane-*d*₁₂, and cyclohexene-*d*₁₀ + cyclohexane-*d*₁₂. The initial reactant concentrations (in molecule cm⁻³ units) were: cyclohexene or cyclohexene-*d*₁₀, $\sim 2.4 \times 10^{13}$; cyclohexane, $\sim 2.4 \times 10^{15}$; or cyclohexane-*d*₁₂, $\sim 3.6 \times 10^{15}$; and two additions of 50 cm³ volume of O₃ in O₂ diluent were made to the chamber. The water vapor concentration was $\sim 3.4 \times 10^{16}$ molecule cm⁻³ (~5% relative humidity). In additional experiments, $\sim 2.4 \times 10^{13}$ molecule cm⁻³ of butanal was added to the cyclohexene (or cyclohexene-*d*₁₀)/cyclohexane/air mixture (at ~5% relative humidity) prior to reaction to investigate whether the butanal intercepted the Criegee intermediate.

FT-IR Analyses. Experiments were carried out in which cyclohexene and cyclohexene-*d*₁₀ were reacted with O₃, both in the presence and absence of cyclohexane as an OH radical scavenger, with analyses by *in situ* FT-IR spectroscopy. The initial concentrations (in units of molecule cm⁻³) were cyclo-

hexene or cyclohexene-*d*₁₀, $(4.77\text{--}4.92) \times 10^{14}$; O₃, 1.47×10^{14} ; and in certain experiments, cyclohexane, 9.5×10^{16} . The reactants were mixed for 3 min using two magnetically coupled Teflon-coated fans, including an ~ 0.5 min injection time for O₃. FT-IR spectra were recorded every 2.5 min with a path length of 62.9 m and a full width at half-maximum resolution of 0.7 cm^{-1} .

The following IR absorption bands with sharp Q branches (cm^{-1}) were used for quantitative measurements: cyclohexene, 1140; cyclohexene-*d*₁₀, 1082; HC(O)OH, 1105; and DC(O)OH, 1143. Calibrated reference spectra of DC(O)OH were obtained by introducing 0.241 g of DC(O)OH into air at atmospheric pressure in the 5800 L chamber, recording the spectra at a path length of 5.59 m for 30 min with 5-min intervals, and correcting the concentrations on the basis of the measured decay rate of $1.90 \times 10^{-3}\text{ min}^{-1}$. A similar procedure was used for the calibration for anhydrous HC(O)OH, obtained from a sample of 90.6% HC(O)OH solution in H₂O which was dried over anhydrous CaSO₄.

Chemicals. The chemicals used and their stated purities were: cyclohexene (HPLC grade), Fisher Scientific; 1,2-butanediol (99%), 2,3-butanediol (98%), 1,3-butanediol (99+%), cyclohexane-*d*₁₂ (99.5 atom % D), glutaraldehyde (50 wt %), 1-hydroxy-2-butanone (95%), 3-hydroxy-2-butanone, *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (98+%), and pentanal (99%), Aldrich Chemical Co.; cyclohexene (99%), Chem Samples; cyclohexene-*d*₁₀ (98 atom % D), Isotec Inc; 4-hydroxy-2-butanone (95+%), TCI America; HC(O)OH (90.6%), Baker Analyzed Reagent; and DC(O)OH (95wt % in water), Aldrich/Isotec. O₃ in O₂ diluent was prepared as needed using a Welsbach T-408 ozone generator.

Results

Measurement of OH Radical Yields. In addition to investigating the formation of OH radicals from the reactions of O₃ with cyclohexene and cyclohexene-*d*₁₀, we also studied the reactions of O₃ with propene, propene-*d*₆, α -pinene and 2,3-dimethyl-2-butene to investigate the effect of deuteration on the propene reaction and compare the measured OH radical formation yields for propene, α -pinene and 2,3-dimethyl-2-butene with previous literature data.^{10,18–24} Plots of the amounts of 3-hydroxy-2-butanone formed against the amounts of cyclohexene and cyclohexene-*d*₁₀ reacted are shown in Figure 1, and the OH (or OD) radical formation yields obtained for the alkenes studied are given in Table 1.

GC-FID and FT-IR Analyses. In agreement with the previous studies of Hatakeyama et al.,⁵ Grosjean et al.,²⁵ and Kalberer et al.,⁷ pentanal was observed from the O₃ reaction with cyclohexene. Plots of the amounts of pentanal and pentanal-*d*₁₀ formed against the amounts of cyclohexene and cyclohexene-*d*₁₀ reacted are shown in Figure 2. Least-squares analyses of these data lead to formation yields of pentanal from cyclohexene and pentanal-*d*₁₀ from cyclohexene-*d*₁₀ of 0.236 ± 0.018 and 0.164 ± 0.014 , respectively, where the indicated errors are two least-squares standard deviations combined with estimated uncertainties in the GC-FID response factors for cyclohexene and pentanal (or their deuterated analogues) of $\pm 5\%$ each.

In situ FT-IR analyses of reacted O₃/cyclohexene/cyclohexane/air and O₃/cyclohexene-*d*₁₀/cyclohexane/air mixtures showed total consumption of the O₃ introduced within 4 min of mixing in all cases. In the cyclohexene reaction in the absence of added cyclohexane, $1.47 \times 10^{14}\text{ molecule cm}^{-3}$ of O₃ consumed $2.18 \times 10^{14}\text{ molecule cm}^{-3}$ of cyclohexene, with a 2.5% yield of HC(O)OH which gradually increased to 3.2% after a period of

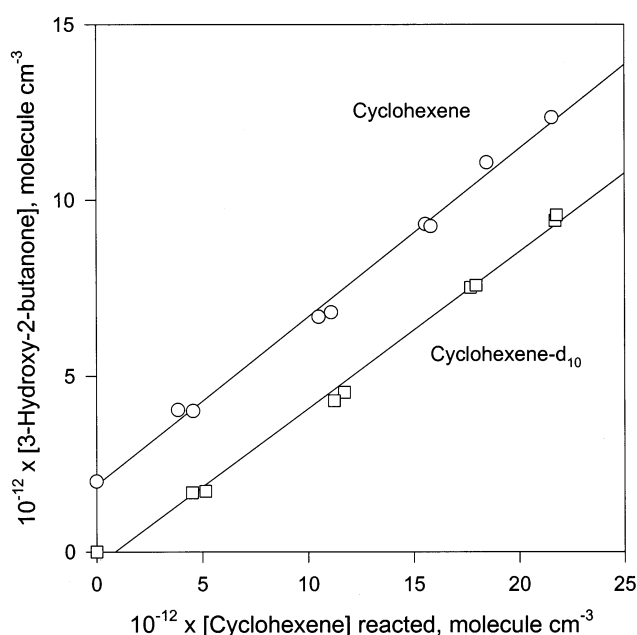


Figure 1. Plots of the amounts of 3-hydroxy-2-butanone formed against the amounts of cyclohexene and cyclohexene-*d*₁₀ reacted with O₃, in the presence of sufficient 2,3-butanediol to scavenge >95% of the OH radicals formed. The 3-hydroxy-2-butanone data from the cyclohexene reaction have been displaced vertically by $2.0 \times 10^{12}\text{ molecule cm}^{-3}$ for clarity.

TABLE 1: Measured OH Radical Formation Yields from Reactions of O₃ with Selected Alkenes at Atmospheric Pressure Using 2,3-Butanediol as the Radical Scavenger, Together with Recent Literature Data

alkene	OH radical formation yield		
	this work ^a	literature	reference
cyclohexene	0.54 ± 0.08	0.54 ± 0.13	Fenske et al. ¹⁰
cyclohexene- <i>d</i> ₁₀	0.50 ± 0.07		
propene	0.40 ± 0.06	0.35 ± 0.07	Paulson et al. ¹⁸
		0.32 ± 0.08	Rickard et al. ¹⁹
		$0.34^{+0.03}_{-0.06}$	Neeb and Moortgat ²⁰
		0.33 ± 0.07	Fenske et al. ²¹
		0.37 ± 0.08	Fenske et al. ²¹
propene- <i>d</i> ₆	0.27 ± 0.04		
α -pinene	0.86 ± 0.13	0.76 ± 0.11	Chew and Atkinson ¹¹
		0.70 ± 0.17	Paulson et al. ²²
		0.83 ± 0.21	Rickard et al. ¹⁹
		0.91 ± 0.23	Siese et al. ²³
2,3-dimethyl-2-butene	1.07 ± 0.16	0.80 ± 0.12	Chew and Atkinson ¹¹
		0.89 ± 0.22	Rickard et al. ¹⁹
		0.99 ± 0.18	Fenske et al. ²¹
		1.00 ± 0.25	Siese et al. ²³
		0.91 ± 0.14	Orzechowska and Paulson ²⁴

^a Indicated errors are two least squares standard deviations combined with estimated uncertainties in the GC-FID response factors for the alkene and 3-hydroxy-2-butanone of $\pm 5\%$ each.

34 min. HCHO was not detected as a product. In the cyclohexene reaction in the presence of sufficient cyclohexane to scavenge >95% of the OH radicals formed, $1.47 \times 10^{14}\text{ molecule cm}^{-3}$ of O₃ consumed $1.62 \times 10^{14}\text{ molecule cm}^{-3}$ of cyclohexene, with a 3.5% yield of HC(O)OH which increased to 4.4% after 17 min. In the cyclohexene-*d*₁₀ reaction in the absence of an OH radical scavenger, $1.47 \times 10^{14}\text{ molecule cm}^{-3}$ of O₃ consumed $2.19 \times 10^{14}\text{ molecule cm}^{-3}$ of cyclohexene-*d*₁₀ and showed a 0.8% yield of DC(O)OH which increased to

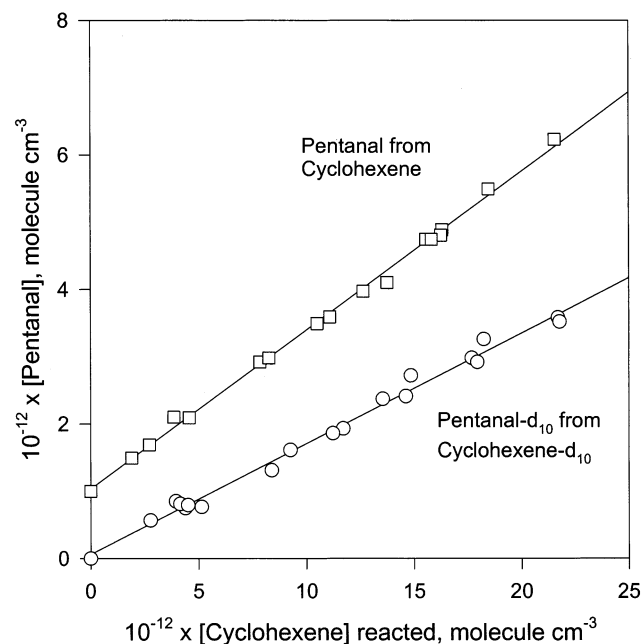


Figure 2. Plots of the amounts of pentanal and pentanal- d_{10} formed against the amounts of cyclohexene and cyclohexene- d_{10} , respectively, reacted with O_3 , in the presence of sufficient cyclohexane or 2,3-butanediol to scavenge $>95\%$ of the OH radicals formed. The pentanal data from the cyclohexene reaction have been displaced vertically by 1.0×10^{12} molecule cm^{-3} for clarity.

1.0% after 10 min. DC(O)OD, which has a sharp Q-branch absorption at 1171 cm^{-1} (the equivalent of the 1143 cm^{-1} absorption of DC(O)OH 26) was not observed; it is expected that the labile D atom of DC(O)OD rapidly undergoes D/H exchange with the water vapor present in the chamber. 27 In the cyclohexene- d_{10} reaction with added cyclohexane, 1.47×10^{14} molecule cm^{-3} of O_3 consumed 1.80×10^{14} molecule cm^{-3} of cyclohexene- d_{10} , and resulted in a 1.6% yield of DC(O)OH which increased to 2.2% after 10 min.

API-MS Analyses. API-MS spectra were obtained from the reactions of O_3 with cyclohexene and cyclohexene- d_{10} , each in the presence of sufficient cyclohexane and cyclohexene- d_{12} to scavenge $>91\%$ (added cyclohexane) or $>86\%$ (added cyclohexene- d_{12}) of the OH radicals formed from the O_3 reactions. The use of cyclohexane and cyclohexene- d_{12} as OH radical scavengers allowed the products formed from the O_3 reactions with cyclohexene and cyclohexene- d_{10} to be differentiated from those formed from the reactions of OH radicals with cyclohexane and cyclohexene- d_{12} . Thus, Figure 3 shows API-MS spectra from reacted O_3 /cyclohexene/cyclohexane/air and O_3 /cyclohexene- d_{10} /cyclohexane/air mixtures using protonated water clusters as the reagent ion, with the ion peaks arising from the reaction of OH radicals with cyclohexane being noted by asterisks. Analysis of the API-MS spectra from the various combinations of reactions showed the products listed in Table 2 from the reactions of O_3 with cyclohexene and cyclohexene- d_{10} .

The most intense ion peaks from pentanal and pentanal- d_{10} were those at $[M+H+H_2O]^+$ at 105 and 115 u, respectively, and an API-MS/MS CAD "product ion" spectrum of the weak 87 u ion peak from the cyclohexene reaction was identical to that of an authentic standard of pentanal. An API-MS/MS CAD "product ion" spectrum of the 101 u ion peak in the cyclohexene reaction in the presence of cyclohexane- d_{12} (the reaction of O_3 with cyclohexene in the presence of cyclohexane leads to a 101 u ion peak from cyclohexanol formed from cyclohexene 9) was identical to that of an authentic standard of glutaraldehyde. The

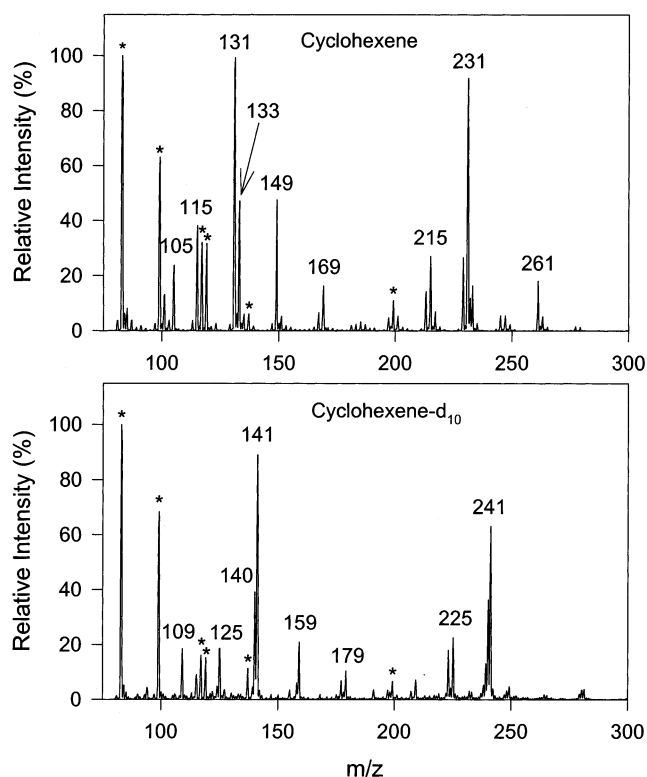


Figure 3. API-MS spectra (using $H_3O^+(H_2O)_n$ as the reagent ion) of reacted O_3 /cyclohexene/cyclohexane/air and O_3 /cyclohexene- d_{10} /cyclohexane/air mixtures. The ion peaks arising from the reaction of OH radicals with cyclohexane are noted by asterisks. For the identities of the major ion peaks see Table 2.

ion peaks at 115 and 125 u in the cyclohexene and cyclohexene- d_{10} reactions, respectively, are attributed to adipaldehyde (see Table 2).

An API-MS/MS CAD "product ion" spectra of the protonated molecular weight 130 and 140 products from the cyclohexene and cyclohexene- d_{10} reactions, respectively, are shown in Figure 4. The CAD spectra reveal that these are analogous products, with the 131 u ion peak from the cyclohexene reaction showing losses of H_2O , $2H_2O$, H_2O+CO , and $2H_2O+CO$, while the 141 u ion peak from the cyclohexene- d_{10} reaction shows losses of $HDO+CO$ and $HDO+D_2O+CO$. These fragmentation patterns suggest the presence of three oxygens, and the presence of 10 deuteriums in the cyclohexene- d_{10} reaction product is consistent with a secondary ozonide.

Figure 5 shows that the 133 u ion peak from the cyclohexene reaction has losses of H_2O , 34 (H_2O_2) and H_2O+CO , while the 140 u ion peak from the cyclohexene- d_{10} reaction has losses of H_2O , H_2O_2 , and $H_2O/HDO+CO$. Particularly interesting (and allowing identification of the 140 u ion peak in the cyclohexene- d_{10} reaction as the analogue to the 133 u ion peak in the cyclohexene reaction) is the loss of a 34 mass unit fragment (H_2O_2) in both cases. Loss of H_2O_2 is indicative of the presence of an OOH group and, because OD (and OOD) groups undergo rapid D/H exchange, 28,29 these losses of H_2O and H_2O_2 are indicative of products containing OOH and OOD groups. Therefore, the products of molecular weight 132 and 139 from the cyclohexene and cyclohexene- d_{10} reactions, respectively, have formula of $C_5H_7O_2(OOH)$ and $C_5D_7O_2(OOH)$, respectively.

Addition of butanal to the reactant mixtures resulted in changes in the post-reaction API-MS spectra. However, at least qualitatively these changes were due to the formation of heterodimers of protonated butanal and the protonated butanal dimer with reaction products. Thus, for example, in a reacted

TABLE 2: Mass Spectral Evidence for Products Formed from the Gas-Phase Reactions of O₃ with Cyclohexene and Cyclohexene-*d*₁₀ in the Presence of an OH Radical Scavenger

O ₃ + cyclohexene			O ₃ + cyclohexene- <i>d</i> ₁₀		
product (MW)	API ^a (see Figure 3)	SPME oximes ^b	product (MW)	API ^c (see Figure 3)	SPME oximes ^d
pentanal (86) CH ₃ CH ₂ CH ₂ CH ₂ CHO	[M+H] ⁺ = 87 [M+H+H ₂ O] ⁺ = 105	[M+H] ⁺ = 282 ^e (2 isomers)	pentanal- <i>d</i> ₁₀ (96) CD ₃ CD ₂ CD ₂ CD ₂ CDO	[M+H] ⁺ = 97 [M+H+H ₂ O] ⁺ = 115	[M+H] ⁺ = 292 [M+H] ⁺ (with H/D exchange) = 293
glutaraldehyde (100) HC(O)(CH ₂) ₃ CHO	[M+H] ⁺ = 101 ^f	[M+H] ⁺ = 491 ^e (dioxime)	glutaraldehyde- <i>d</i> ₈ (108) DC(O)CD ₂ CD ₂ CD ₂ CDO	[M+H] ⁺ = 109	[M+H] ⁺ (with H/D exchange) = 500 [M+H] ⁺ (with 2 H/D exchanges) = 501
adipaldehyde (114) HC(O)(CH ₂) ₄ CHO	[M+H] ⁺ = 115	[M+H] ⁺ = 505 (dioxime)	adipaldehyde- <i>d</i> ₁₀ (124) DC(O)(CD ₂) ₄ CDO	[M+H] ⁺ = 125	[M+H] ⁺ (with H/D exchange) = 516 [M+H] ⁺ (with 2 H/D exchanges) = 517
secondary ozonide (130) C ₆ H ₁₀ O ₃	[M+H] ⁺ = 131 ^g [M+H+H ₂ O] ⁺ = 149		secondary ozonide (140) C ₆ D ₁₀ O ₃	[M+H] ⁺ = 141 ^g [M+H+H ₂ O] ⁺ = 159	
C ₆ H ₁₀ O ₃ (130) ^h		[M+H] ⁺ = 326 [M+H-H ₂ CO ₂] ⁺ = 280	C ₆ D ₁₀ O ₃ (140)		[M+H] ⁺ = 336 [M+H] ⁺ (with H/D exchange) = 337 [M+H-HDCO ₂] ⁺ = 289
peracid (132) C ₅ H ₇ O ₂ (OOH)	[M+H] ⁺ = 133 ⁱ		peracid (139) C ₅ D ₇ O ₂ (OOH) ^j	[M+H] ⁺ = 140 ⁱ	
hydroxydicarbonyl (130) HC(O)(CH ₂) ₃ CH(OH)CHO ^k		[M+H] ⁺ = 326 [M+H-H ₂ O] ⁺ = 308 (monooxime) [M+H] ⁺ = 521 [M+H-H ₂ O] ⁺ = 503 (dioxime)	hydroxydicarbonyl (139)		[M+H] ⁺ = 335 [M+H] ⁺ (with H/D exchange) = 336 [M+H-H ₂ O] ⁺ = 317 (monooxime) [M+H] ⁺ (with H/D exchange) = 531 [531-H ₂ O] ⁺ = 513 [531-HDO] ⁺ = 512 (dioxime)
hydroxycarbonyl or oxo-acid (116)		[M+H] ⁺ = 312 [M+H-H ₂ O] ⁺ = 294	hydroxycarbonyl or oxo-acid (123)		[M+H] ⁺ = 319 [M+H] ⁺ (with H/D exchange) = 320 [319-H ₂ O/HDO] ⁺ and [320-HDO] ⁺ = 300 and 301

^a The high mass peaks in Figure 3 (top) are those of homo- and heterodimers. For example, 261 = 130+130+H, 215 = 114+100+H, 231 = 130+100+H, and 169 = 100+86+H-H₂O. Note that the major products from the cyclohexane scavenger reaction with the OH radical are cyclohexanone (MW 98) and cyclohexanol (MW 100) and these may participate in the formation of heterodimers. ^b Forming an oxime derivative adds 195 mass units to the molecular weight; a diderivative adds 390 units. ^c The high mass peaks in Figure 3 (bottom) are those of homo- and heterodimers. For example, 225 = 124+100+H, 241 = 140+100+H, and 179 = 100+96+H-H₂O. Note that the major products from the cyclohexane scavenger reaction with the OH radical are cyclohexanone (MW 98) and cyclohexanol (MW 100) and these participate in the formation of heterodimers. ^d D/H exchange occurs in ion source. Forming an oxime derivative adds 195 mass units to the molecular weight; a diderivative adds 390 units. ^e GC retention times and mass spectra verified with standard compounds. ^f See text for discussion of reaction with cyclohexane-*d*₁₂ which allowed unambiguous identification of glutaraldehyde. ^g See Figure 4 for CAD spectra. ^h Possibly the secondary ozonide which was sampled by the SPME, with decomposition on the fiber to form an oxo-acid which was then derivatized and analyzed as its oxime (see text). ⁱ See Figure 5 for CAD spectra. ^j OD/OH exchange occurs, presumably with water in the chamber. ^k Tentative identification (see Scheme 3).

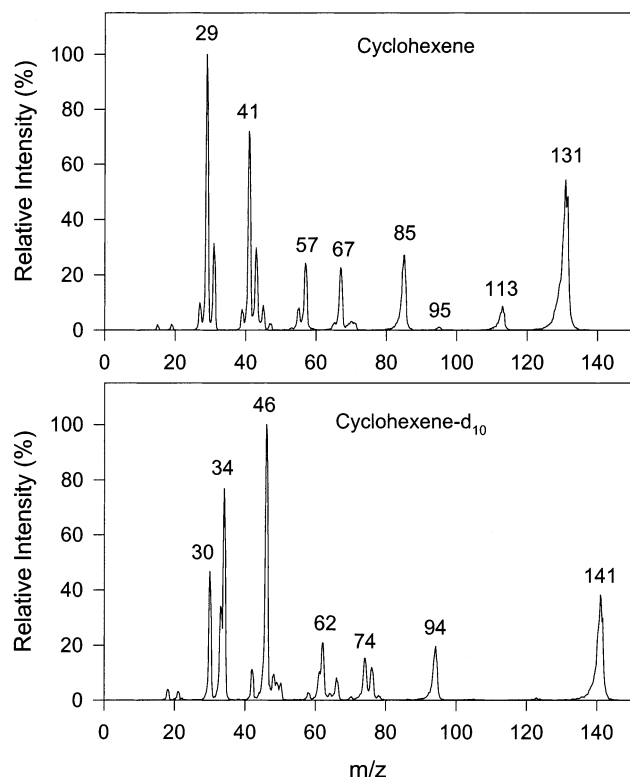
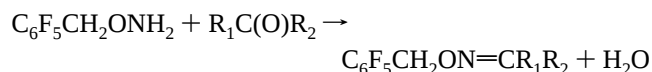


Figure 4. API-MS/MS CAD "product ion" spectra (using $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ as the reagent ion) of the 131 and 141 u ion peaks observed in the reactions of O_3 with cyclohexene and cyclohexene- d_{10} reactions, respectively. Cyclohexane was present to scavenge OH radicals.

O_3 /cyclohexene/cyclohexane/butanal/air mixture compared to a reacted O_3 /cyclohexene/cyclohexane/air mixture the ion peaks of the molecular weight 114 and 130 products (which are believed to involve reactions of the thermalized Criegee intermediate; see below) and their protonated homo- and heterodimers at 115, 131, 149, 215, 231, and 261 u (see Table 2) decreased in the presence of butanal and were replaced (at least in part) by ion peaks at 217 u ($[\text{114}+\text{butanal}+\text{H}]^+$) and 275 u ($[\text{130}+\text{butanal}+\text{butanal}+\text{H}]^+$) in the presence of butanal in the reactant mixture. In particular, no evidence for any significant formation of the secondary ozonide arising from reaction of the Criegee intermediate $\text{HC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOO}$ (and its deuterated analog) with butanal was observed (the protonated secondary ozonides being at 203 and 213 u, respectively).

GC-MS Analyses of PFBHA Derivatives. In two experiments, PDMS/DVB SPME fibers precoated with PFBHA were exposed in the chamber to cyclohexene and cyclohexene- d_{10} reaction products. Oxime derivatives are formed from carbonyl-containing compounds through the reaction.



Utilizing GC-MS with isobutane chemical ionization, generally intense protonated molecules $[\text{M}+\text{H}]^+$ and small adduct ions at $[\text{M}+41]^+$ are observed, where the molecular mass M of the oxime is 195 mass units greater than the weight of the carbonyl, or in the case of a dicarbonyl forming a dioxime, 390 mass units higher. Note that *Z* and *E* configurations are sometimes present and resolved.

The oximes observed are listed in Table 2. Pentanal and glutaraldehyde were identified based on matching the GC

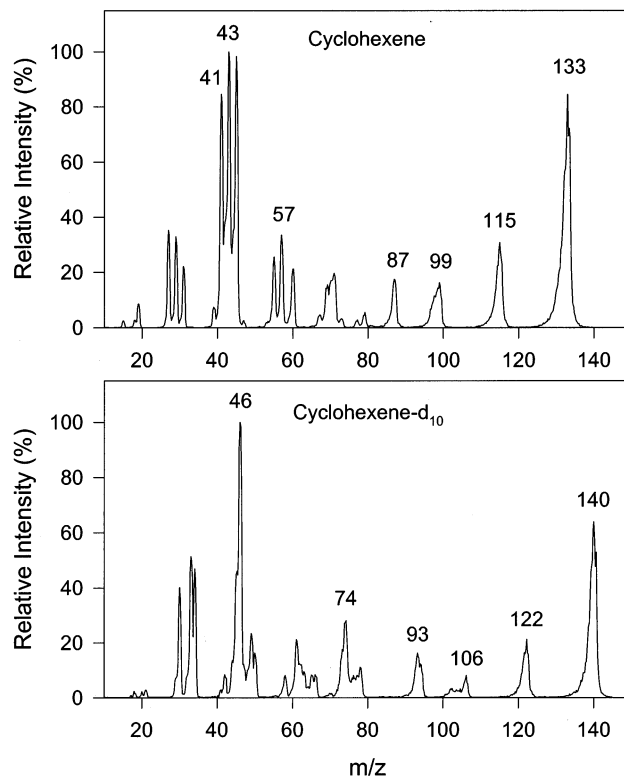


Figure 5. API-MS/MS CAD "product ion" spectra (using $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ as the reagent ion) of the 133 and 140 u ion peaks observed in the reactions of O_3 with cyclohexene and cyclohexene- d_{10} reactions, respectively. Cyclohexane was present to scavenge OH radicals. Note the presence of fragment ions at 99 and 106 u from the cyclohexene and cyclohexene- d_{10} reactions, respectively, indicating a loss of H_2O_2 in both cases.

retention times and mass spectra with those of authentic standards. Note that two isomers of the oxime from pentanal were formed and both carbonyls in glutaraldehyde were derivatized, with only a trace of the singly derivatized compound oxime being observed. The corresponding peaks from the cyclohexene- d_{10} reaction eluted from the GC column a few seconds earlier than the cyclohexene products. The presence of the apparent molecular ion of glutaraldehyde- d_8 at 500 u rather than the predicted 499 u, with an ion peak also observed at 501 u, must be attributed to H/D exchange in the ion trap source, which is subject to secondary ion-molecule reactions.³⁰

The SPME analysis confirmed the presence of two carbonyl groups in the molecular weight 114 compound attributed to adipaldehyde in the API analyses. A large oxime peak corresponding to a molecular weight 130 compound was also observed from the cyclohexene reaction, and in contrast to the oximes of pentanal, glutaraldehyde, and adipaldehyde which showed almost no fragmentation, the base peak in the spectrum was due to a loss of H_2CO_2 from the $[\text{M}+\text{H}]^+$ molecular ion. As noted in Table 2, the corresponding peak from the cyclohexene- d_{10} reaction suggested 10 deuteriums and a base peak due to loss of HDCO_2 from the $[\text{M}+\text{H}]^+$ ion (or loss of D_2CO_2 from the $[\text{M}+\text{D}]^+$ ion). It is possible that this oxime peak is due to SPME sampling of the secondary ozonide, with decomposition of the secondary ozonide on the SPME fiber to an oxo-acid which was then derivatized and analyzed as its oxime.

Significantly smaller peaks corresponding to two carbonyl-containing compounds of molecular weight 116 and 130 were also observed in the SPME analysis. For the molecular weight 130 product, both mono- and dioxime derivatives were observed,

indicating a dicarbonyl. The oximes gave fragments corresponding to a loss of H₂O and, in the cyclohexene-*d*₁₀ reaction, a loss of H₂O and HDO, suggesting³¹ that this product is a hydroxydicarbonyl and possibly that shown in Scheme 3 [HC(O)CH₂CH₂CH₂CH(OH)CHO]. For the molecular weight 116 carbonyl-containing product only a monooxime derivative was observed. The oxime gave a fragment corresponding to a loss of H₂O and, in the cyclohexene-*d*₁₀ reaction, a loss of H₂O and HDO, suggesting that this product is a hydroxycarbonyl³¹ or possibly an oxo-acid (without standards no conclusive identification is possible).

The presence of a small hydroxydicarbonyl of molecular weight 130 (as noted, possibly HC(O)CH₂CH₂CH₂CH(OH)CHO) is not inconsistent with the API-MS/MS data shown in Figures 4 and 5. In Figure 4 (top) the [M+H]⁺ = 131 u ion peak from the cyclohexene reaction may be attributed primarily to the protonated secondary ozonide plus a small amount of the protonated hydroxydicarbonyl, while the [M+H]⁺ = 141 u ion peak (Figure 4, bottom) from the cyclohexene-*d*₁₀ reaction is solely due to the protonated secondary ozonide-*d*₁₀. In Figure 5 (top) the [M+H]⁺ = 133 u ion peak from the cyclohexene reaction may be attributed solely to the protonated peracid, while the [M+H]⁺ = 140 u ion peak (Figure 5, bottom) from the cyclohexene-*d*₁₀ reaction is due primarily to the protonated peracid-*d*₇ plus a small amount of the protonated hydroxydicarbonyl-*d*₉.

Discussion

On the basis of our GC-FID, GC-MS, API-MS, and FT-IR analyses, the gas-phase products observed from the reaction of O₃ with cyclohexene in the presence of an OH radical scavenger are pentanal (23.6 ± 1.8%), OH radicals (54 ± 8%), formic acid (3.5% initial yield), glutaraldehyde [HC(O)CH₂CH₂CH₂CHO], adipaldehyde [HC(O)CH₂CH₂CH₂CHO], a C₆H₁₀O₃ product which is attributed to the secondary ozonide, a C₅H₇O₂-(OOH) product, a hydroxydicarbonyl of molecular weight 130 (possibly HC(O)CH₂CH₂CH₂CH(OH)CHO), and a hydroxycarbonyl or possibly oxo-acid of molecular weight 116. As evident from Table 1, the OH radical formation yield measured here from the cyclohexene reaction is in excellent agreement with the value of Fenske et al.¹⁰ Furthermore, our present OH radical formation yields from the reactions of O₃ with propene, α-pinene and 2,3-dimethyl-2-butene are in good agreement with recent literature data^{18–24} (Table 1), indicating that 2,3-butanediol can be used to determine OH radical yields from the amounts of 3-hydroxy-2-butanone formed.

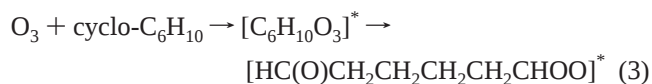
The deuterium isotope ratios *k_H/k_D* for the OH (or OD) radical yields from the reactions of O₃ with propene and cyclohexene are 1.48 ± 0.31 and 1.08 ± 0.22, respectively. These are fairly close to unity (especially for the cyclohexene reaction) and presumably reflect the fractions of the Criegee intermediates formed in the *syn*-configuration (see below) together with the effect of deuterium substitution on the branching ratios for the various reaction channels.

Our pentanal yield from cyclohexene (23.6 ± 1.8%) is a factor of 1.5 higher than the yield reported by Grosjean et al.²⁵ of 15.6 ± 0.4%. A similar discrepancy occurs for the reaction of O₃ with cyclopentene where we previously measured a butanal yield of 19.5 ± 2.7%,³² compared to the yield of 12.0 ± 0.1% reported by Grosjean and Grosjean.³³ Pentanal yields have also been reported by Hatakeyama et al.⁵ (17.2 ± 1.7% relative to the amount of cyclohexene consumed in the absence of an OH radical scavenger; this corresponds to a

pentanal yield from the O₃ reaction with cyclohexene of 26.5 ± 3.0% assuming that all of the OH radicals formed reacted with the cyclohexene and did not lead to pentanal formation, in agreement with our pentanal yield) and by Kalberer et al.⁷ (17.0 ± 9.4%, in the presence of an OH radical scavenger).

Our yield of HC(O)OH from the reaction of O₃ with cyclohexene of 2.5–3.2% in the absence of an OH radical scavenger is similar to that of 3.7% calculated from the spectrum shown by Niki et al.,³⁴ but is significantly lower than the yield of 12 ± 1% reported by Hatakeyama et al.⁵ In agreement with previous studies,^{5,34} HCHO was not detected as a reaction product. In the presence of sufficient cyclohexane to scavenge >95% of the OH radicals formed, the HC(O)OH yield from the cyclohexene reaction was initially 3.5%, increasing to 4.4% after 17 min (note that the O₃ was consumed after 4 min), while the yield of DC(O)OH [which, because of rapid OD/OH exchange, could have been formed as DC(O)OD] from the cyclohexene-*d*₁₀ reaction was initially 1.6%, increasing to 2.2% after 10 min. There therefore appears to be a significant deuterium isotope effect on the formic acid yield, of a factor of ~2.0–2.2.

The initial reaction of cyclohexene with O₃ forms the primary ozonide which rapidly decomposes to an energy-rich Criegee intermediate, which theoretical studies show to be a carbonyl oxide and which can exist in a *syn*- or *anti*-configuration (see, for example, Fenske et al.³⁵ and Kroll et al.^{36,37}).



As shown in Scheme 1 (in which identified products are shown in boxes), this Criegee intermediate can be collisionally stabilized, decompose to form CO₂ plus pentanal (possibly through the ester channel), and, for the *syn*-intermediate, isomerize to a hydroperoxide which then eliminates an OH radical.^{1–3,35–37} The recent studies of Kroll et al.^{36,37} and Fenske et al.³⁵ show that thermalized Criegee intermediates can also undergo isomerization with subsequent decomposition to form an OH radical (plus organic radical coproduct), as also indicated in Scheme 1 for the *syn*-intermediate.

The thermalized Criegee intermediate may also react with water vapor present to form an α-hydroxyhydroperoxide, which may be thermally stable or decompose to either 6-oxohexanoic acid [HC(O)CH₂CH₂CH₂CH₂C(O)OH] plus H₂O or to adipaldehyde [HC(O)CH₂CH₂CH₂CHO] plus H₂O₂ (Scheme 2).^{38,39} Our product data indicate that decomposition and/or isomerization of the Criegee intermediate to form pentanal (plus CO₂) and an OH radical plus organic radical coproduct account for 78 ± 9% of the reaction pathways. Adipaldehyde can be formed from reaction of the thermalized Criegee intermediate (presumably the *anti*-intermediate, with the *syn*-intermediate decomposing to an OH radical) with water vapor (Scheme 2). The product of molecular weight 130 from cyclohexene and 140 from cyclohexene-*d*₁₀ observed by API-MS (and possibly by SPME after decomposition) is consistent with this product being the secondary ozonide formed by recyclization of the Criegee intermediate (Scheme 1).

Addition of ~2.4 × 10¹³ molecule cm⁻³ of butanal to the reactant mixture resulted in no marked changes in the products formed, as deduced from the API-MS spectra. In particular, no

The organic coproduct to the OH radical, anticipated to be the HC(O)CH₂CH₂CH₂C•HCHO radical (Scheme 1) will add O₂ and the resulting peroxy radical will react with HO₂ and organic peroxy (RO₂•) radicals as shown in Scheme 3,^{2,3} leading to the formation of a series of multifunctional products (Scheme 3), including glutaraldehyde and the hydroxydicarbonyl HC(O)CH₂CH₂CH₂CH(OH)CHO.

The formation route to the observed product of formula C₅H₇O₂(OOH) [molecular weight 132] is less obvious. On the basis of the observed formation of exclusively ¹⁸O-labeled HC-(¹⁸O)¹⁸OH from the reaction of ¹⁸O₃ with cyclohexene (in the absence of an OH radical scavenger), Hatakeyama et al.⁵ postulated that HC(O)OH arises through the reaction sequence involving the HC(O)CH₂CH₂CH₂CH₂CH(O•)O• and •OCCH₂CH₂CH₂CH₂CH(OH)O• species (i.e. via the ester channel pathway in Scheme 1). The coproduct to HC(O)OH is then postulated⁵ to be the •OCCH₂CH₂CH₂C•H₂ biradical which reacts, as proposed by Jenkin et al.,⁴¹ to form the •OOC(O)CH₂CH₂CH₂CHO species (Scheme 1), then leading to the molecular weight 132 peracid HOOC(O)CH₂CH₂CH₂CHO. The corresponding products in the cyclohexene-*d*₁₀ reaction will then be (after OOD/OOH exchange) the molecular weight 139 peracid HOOC(O)CD₂CD₂CD₂CDO. Clearly, the specific identify and formation route of the observed molecular weight 132 C₅H₇O₂(OOH) product shown in Scheme 1 is speculative, but the number of other possibilities seems limited. This pathway would also lead to 5-oxopentanoic acid of molecular weight 116, which may possibly be the product of this molecular weight observed in the SPME analysis. It should also be noted that the formic acid formation yield was observed to increase somewhat with increasing extent of reaction, suggesting in addition to a "prompt" formation route the existence of a slow secondary formation pathway for formic acid.

The gas-phase products observed here are consistent with the aerosol-phase products observed by Ziemann.⁸ In particular, Ziemann⁸ observed aerosol-phase products attributed to diacyl peroxides formed from reactions of peroxyacyl radicals of structure HC(O)(CH₂)_nC(O)OO• and HOC(O)(CH₂)_nC(O)OO•, where *n* = 3 and 4, consistent with our observation of the molecular weight 132 product suggested to be the peracid HOOC(O)CH₂CH₂CH₂CHO and formed from the acyl peroxy radical HC(O)(CH₂)₃C(O)OO• (Scheme 1).

Acknowledgment. The authors thank the California Air Resources Board (CARB) for supporting this research (Contract No. 99-330), and thank Dr. Paul J. Ziemann for helpful discussions. While this research has been funded by the CARB, the results and content of this publication do not necessarily reflect the views of the CARB.

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