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Aerosol Formation in the Cyclohexene-Ozone System

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Atmospheric oxidation of certain volatile organic compounds can lead to products of sufficiently low vapor pressure that the products partition into the aerosol phase, producing what is termed secondary organic aerosol. Cyclohexene has long been known to produce aerosol upon photooxidation. In this study, we obtain molecular product information especially for those species that partition between the gas and particle phases. Compounds identified in the aerosol phase include hydroxyglutaric acid, adipic acid, and hydroxyadipic acid. In accord with previous studies, pentanal is found to be the predominant identified gas-phase products, at a molar yield of 17%. Possible explanations for the presence of relatively high vapor pressure compounds in the aerosol phase are advanced.

Introduction

Volatile organic compounds, when photooxidized in the atmosphere, can lead to products that have sufficiently low vapor pressure to partition between the gas and aerosol phases. The fraction of organic particulate matter arising from this path is referred to as secondary organic aerosol (SOA). Parent organic compounds that, upon oxidation, lead to SOA generally contain six or more carbon atoms. While overall yields of SOA have been measured in the laboratory, investigation of aerosol composition at the molecular level have only recently begun to resolve an appreciable fraction of SOA. Molecular identification of SOA is difficult because atmospheric oxidation pathways of $\geq C_6$ compounds lead to a relatively large number of products that are generally highly polar, complicating their analysis. Cyclohexene, a cyclic alkene that is known to produce aerosol upon oxidation, was, in fact, one of the first organic compounds investigated for its aerosol-forming potential. Hatakeyama et al. (*1*) identified pentanedial, 5-oxopentanoic acid, glutaric acid, hexanedial, 6-oxohexanoic acid, and adipic acid as SOA products of cyclohexene oxidation. Gaseous compounds measured included formic acid, pentanal, pentanedial, and hexanedial. Since no actual aerosol measurements were performed in that study, there is no information as to what fraction of the total particle mass was identified. In a later study, Izumi et al. (*2*) measured the aerosol yield of cyclohexene in the presence of ozone and OH radicals in the cyclohexene concentration range between 0.5 and 5 ppm but determined only the total carbon and nitrogen content of the aerosol particles. Grosjean et al. (*3*) measured gas-phase products of the cyclohexene-ozone reaction, in the presence of an OH scavenger (cyclohexane), and found pentanal as a principal oxidation product.

TABLE 1. Experimental Conditions

experiment	O_3 (initial) [ppb]	cyclohexene (initial) [ppb]	cyclohexene (final)[a] [ppb]	Δcyclohexene [ppb]	M_o[b] [μg/m^3]	yield[c] [%]
5/13/99a	539	131	1.3	130	43	9.6
5/13/99b	388	87	2.5	85	36	12.3
5/17/99a	634	186	2.8	183	126	20.0
5/17/99b	415	120	3.2	117	43	10.7
5/19/99a	203	48	4.2	44	14	9.3
5/19/99b	1011	137	0[d]	137	36	7.6

[a] Concentration when denuder/filter sampling began. [b] ΔM_o = based on SEMS measurements, assumed $\rho = 1.4$ g/cm^3, see text. [c] Yield = $\Delta M_o/\Delta$cyclohexene. [d] Below detection limit.

The goal of the present paper is to revisit the cyclohexene-ozone system. Cyclohexene-ozone has been selected as a model system because it has been intensively studied, gas-phase products are well-characterized, and a reasonable amount is known about reaction mechanisms in the system. Although cyclohexene is not likely to be an important precursor for secondary organic aerosol in the ambient atmosphere, the cyclohexene-ozone system is highly relevant for its use as a model system that is relatively well understood. We seek molecular identification of gas- and aerosol-phase products, using recently developed methods of derivatization and mass spectrometric detection. Such data will, in the future, serve as a basis for evaluating the ability to predict SOA formation from first principles; that is, if all the semivolatile oxidation products of a parent hydrocarbon were known, together with their physical properties, such as their vapor pressures, then the yield of SOA from that parent molecule could be predicted for any given set of conditions.

Experimental Section

Smog Chamber Experiments. Most of the experimental procedures associated with the Caltech outdoor smog chamber have been described previously (*4*−*6*), and only a brief summary is given here. Reactant concentrations and general experimental conditions for the cyclohexene-O_3 system are given in Table 1. Experiments were performed in the dark in two outdoor Teflon chambers of about 22 m^3 volume each. The temperature for all experiments was maintained at 298 K (±2 K). Before the reactants were introduced into the chambers, $(NH_4)_2SO_4$ seed aerosol, of mean diameter of approximately 100 nm, was injected, at a number concentration of about 10^4 cm^{-3}. Particle number and size measurements were performed with a differential mobility analyzer (Model 3071, TSI, St. Paul, MN) and a condensation nucleus counter (Model 3760, TSI, St. Paul, MN). To prevent OH oxidation by OH generated in alkene-O_3 reactions, CO was added as an OH scavenger (see for example ref *7*), at levels (268 to 1040 ppm) sufficient to ensure that >95% of any OH generated was scavenged. (The current experiments were not designed to measure OH yield from the cyclohexene-O_3 reaction.) Samples for gas- and particle-phase analysis were taken after the hydrocarbon was essentially consumed. The mixing ratio of cyclohexene was measured with a Hewlett-Packard 5890 GC/FID. All experiments were carried out under dry conditions (RH < 5%), so the dependence of product levels on aerosol water was not addressed.

Gas and Particle Sampling. Since many reaction products are present in both gas and particle phases, the sampling

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TABLE 2. Denuder Collection Efficiencies for Individual Cyclohexene/Ozone Reaction Products

reaction product	denuder collection efficiency[a]
oxalic acid	0.95 ± 0.02
malonic acid	0.98 ± 0.01
succinic acid	0.96 ± 0.02
adipic acid	0.98 ± 0.01
glutaric acid	0.99 ± 0.01
4-hydroxy-1-butanal	0.91 ± 0.08[b]
hydroxypentanoic acid	0.99 ± 0.01
hydroxyglutaric acid	0.95 ± 0.02
hydroxyadipic acid	0.93 ± 0.02
6-oxohexanoic acid	0.98 ± 0.03
5-oxopentanoic acid	0.99 ± 0.01
4-oxobutanoic acid	0.98 ± 0.01
1,6-hexanedial	0.99 ± 0.01
1,5-peritanedial	0.98 ± 0.02
1,4-butanedial	0.92 ± 0.06
pentanal	0.77 ± 0.18

[a] Denuder collection efficiencies for individual products are calculated using six sets of samples. [b] Only five data points.

system consisted of a series of two annular denuders (University Research Glassware, Chapel Hill, NC) to remove the gaseous reaction products, followed by a Teflon-coated quartz fiber filter (Pallflex, Putnam, CT), which collected all particles. The first denuder is 40 cm long, and the second is 20 cm long. Both denuders consist of 5 annular channels with 2 mm spacing between channels. An additional denuder was placed behind the filter to trap compounds that might volatilize from the filter during sampling. The gaseous concentration of a compound was calculated from the sum of the amounts found in the first two denuders, and the particle phase concentration was determined from the amounts found on the filter and the third denuder. Samples were taken at a flow rate of 25 L min^{-1} for 1 h resulting in a total sampling volume of 1.5 m^3. We evaluated particle loss to the denuders and found it to be less than 5% by mass. Regarding artifacts from blowing off a compound from a denuder to the gas phase, our experiments showed that two denuders retain more than 99.4% of all compounds with the exception of pentanedial, for which the retention was 95%. The composition of secondary aerosols may include artifacts from filter absorption of gas-phase species that evade denuder collection. The contribution from this effect can be estimated for 1,4-butanedial, the most volatile product detected in the aerosol phase. The first denuder has a collection efficiency for 1,4-butanedial of 92% (Table 2); the two denuders then have a combined collection efficiency of 99.4% for this compound. If the 0.6% of gaseous 1,4-butanedial that escaped collection on the denuders was retained on the filter, this amounted to $0.6\% \times 0.45\% = 0.0027\%$ of the 1,4-butanedial gas-phase yield. The measured aerosol-phase yield of 1,4-butanedial was 0.05% (to be presented subsequently). Thus, only 5% (0.0027/0.05) of the 1,4-butanedial collected on the filter can be attributed to artifact. Further details about denuder coating and preparation are given by Yu et al. (*4*).

Sample Treatment and Analysis. Following elution of the denuders with a dichloromethane/acetonitrile/hexane mixture and extraction of the filter in a Soxhlet apparatus (dichloromethane/acetonitrile mixture), the samples were derivatized with PFBHA (*O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxyamine) and BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide). The derivatization reactions convert polar into less polar compounds, i.e., carbonyl groups react with PFBHA to form oxime derivatives; carboxyl and hydroxyl groups react with BSTFA to form trimethylsilyl derivatives. Sample analysis was performed with a Varian Star 3400/Saturn 2000 gas chromatograph/mass spectrometer in electron ionization and chemical ionization mode. The gas used in the CI mode was methane. Samples were separated in a RTX-5MS column (Restek, Bellefonte, PA).

Most compounds identified were quantified, either with an authentic standard or with surrogate compounds of similar structure. Calibration mixtures that included all standards were produced at five concentrations in the range of 10−50 ng μL^{-1}. Compound specific ions or, in the case of surrogates, mass fragments typical for the functional group were used for quantification of the different compounds. Surrogates were chosen to have the same type and number of functional groups and the same carbon number, if possible. Since the compounds with surrogates were quantified with mass fragments typical for the functional groups, the number of functional groups was important for selection of a surrogate compound.

Recovery experiments to account for losses during sampling were performed by spiking standard mixtures with known amounts of all standard compounds on the denuders and filters. The denuder collection efficiency, defined by the amount of a given compound collected by the two denuders preceding the filter, is shown for each compound in the cyclohexene-O$_3$ system in Table 2. The collection efficiency was > 91% for all compounds, except for pentanal. Because it is expected that pentanal should exist exclusively in the gas-phase, the amount of pentanal found on the filter and on the denuder behind the filter was considered to be part of the gas-phase fraction. Because analytes can be lost to extraction vessels and by evaporation during rotary evaporation, "recovery" refers to the fraction of a compound that is recovered at the end of the treatment process.

Results and Discussion

Aerosol Yield. Figure 1 shows cyclohexene and total particle mass concentrations for experiment 5/13/99a; this behavior is typical of all experiments. Cyclohexene was almost completely consumed within the first 2 h, and the organic particle mass increased correspondingly. Typical aerosol size distributions before the start of the experiment and after particle growth ceased are shown in the insert in Figure 1. The volume of organic aerosol material produced, ΔM_o, was determined from the two size distributions, after accounting for wall losses of particles.

For a wide variety of parent VOCs, the fractional aerosol yield by mass that is Y as a function of ΔM_o, can be fit by assuming two empirical oxidation products *(5, 8)*. Fractional aerosol yields for the six cyclohexene-O$_3$ experiments are given in Table 1. Parameters *(5, 8)* of the two-component best fit correlation to these data are $\alpha_1 = 0.36$, $\alpha_2 = 0.32$, $K_{om,1} = 0.009$ m^3 μg^{-1}, and $K_{om,2} = 0.001$ m^3 μg^{-1}.

Identification of Products. Identified products in the cyclohexene-ozone system are given in Table 3. In the mass spectrometer, derivatized compounds fragment in a characteristic way, as described by Yu et al. (*6*) and LeLacheur et al. (*9*). Compounds with a carbonyl functional group are identified by the mass m/z 181, and those with a carboxylic or hydroxy group show a typical mass fragment at m/z 73 and m/z 75. In addition, the fragments at m/z M − 15, M − 73, M − 89, and M − 117 (M − 117 is a characteristic ion only for carboxyl groups, not for hydroxyl groups), which denote a loss of $[CH_3]$, $[Si(CH_3)_3]$, $[OSi(CH_3)_3]$, and $[C(O)OSi(CH_3)_3]$ from the derivatized molecule, respectively, were used in identification. In the CI mode the fragment M − 89 was often stronger compared to EI mode spectra, where M − 117 was often prominent. Also the molecular ion and the adduct ion, M + 1 and M + 73, were often detected in the CI mode spectra. The fragment m/z 147 was always associated with compounds with two carboxyl or hydroxyl groups, and m/z 117 ($C(O)OSi(CH)_3$) was prominent in spectra of compounds with only one carboxylic group. For compounds with carbonyl

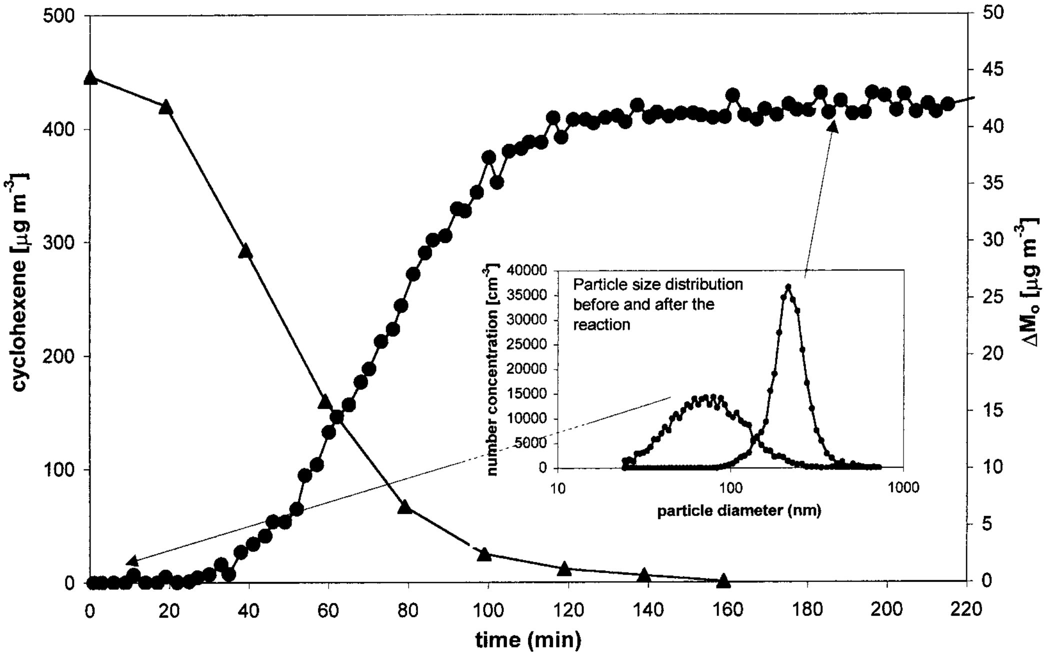


FIGURE 1. Cyclohexene and total aerosol mass concentration ΔM_o as a function of time. As the cyclohexene concentration decreases with time, the organic aerosol mass increases correspondingly. The organic aerosol mass, ΔM_o, is calculated from the difference of the aerosol size distributions at the beginning and end of the reaction, as shown in the insert.

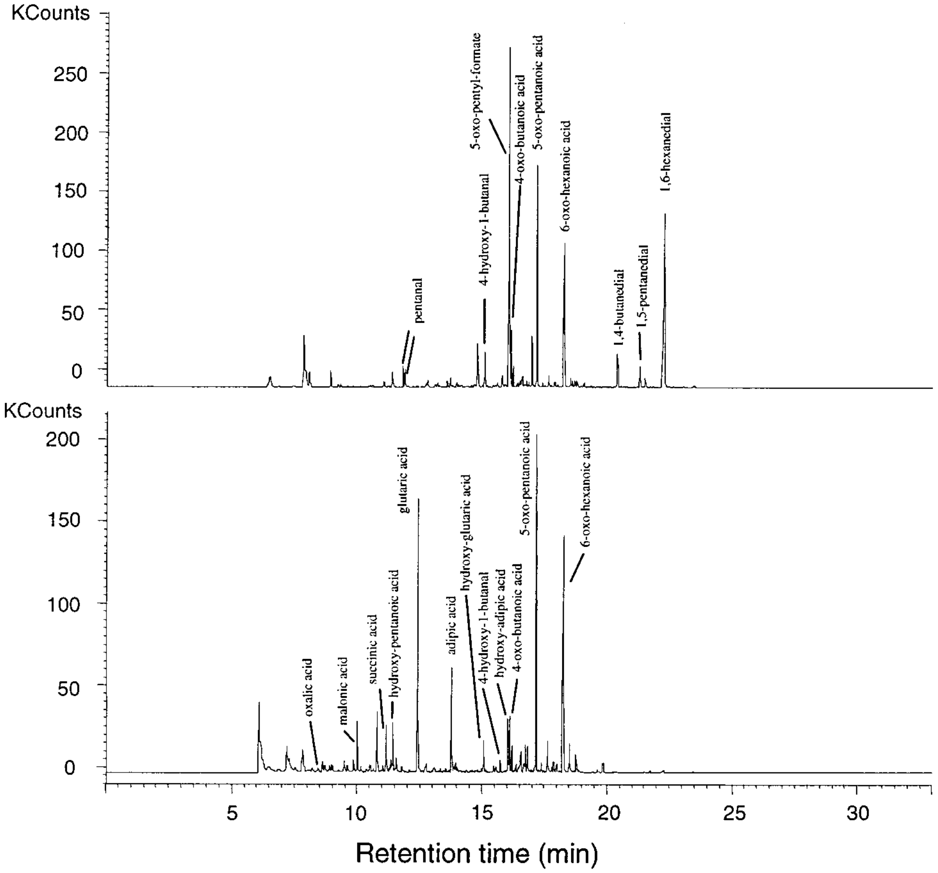
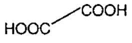
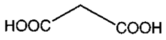
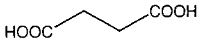
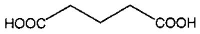
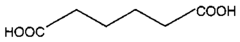
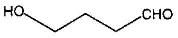
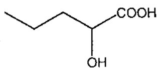
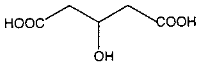
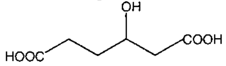
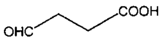
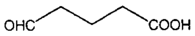
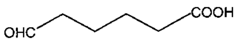
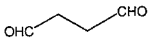
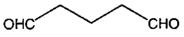
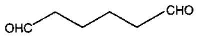
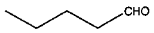
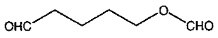


FIGURE 2. Chromatogram of a filter sample: (a) *m/z* 181 chromatogram showing all carbonyl compounds identified and (b) *m/z* 73+75 chromatogram showing the compounds with a carboxylic and/or hydroxy functional group.

groups, the mass fragment M − 197, which results from a loss of [$OCH_2C_6F_5$] from the derivatized molecule, was generally used for identification in the EI mode mass spectrum along with the molecular ion in the CI mode spectrum.

Figure 2a shows the *m/z* 181 ion chromatogram of a filter sample indicating all nine compounds identified in the cyclohexene-O_3 system with a carbonyl group, and Figure 2b shows the *m/z* 73+75 ion chromatogram of the same sample with all 12 compounds identified containing a

TABLE 3. Chemical Structures of Products of the Cyclohexene-Ozone Reaction

Compound	Structure	Molecular weight	Molecular weight of derivative[a]
oxalic acid		90	234
malonic acid		104	248
succinic acid		118	262
glutaric acid		132	276
adipic acid		146	290
4-hydroxy-1-butanal		88	355
2-hydroxy pentanoic acid		118	262
3-hydroxy glutaric acid		148	364
3-hydroxy adipic acid		162	378
4-oxo-butanoic acid		102	369
5-oxo-pentanoic acid		116	383
6-oxo-hexanoic acid		130	397
1,4-butanedial		86	476
1,5-pentanedial		100	490
1,6-hexanedial		114	504
pentanal		86	281
5-oxo-pentyl formate		130	325

[a] Molecular weight for derivative is for full derivatization of all the possible functional groups in the molecule.

carboxylic and/or hydroxyl group. In total, 17 compounds were identified, for eight of which an authentic standard was available, the others identified tentatively by their mass spectra (see Table 4).

Three dialdehydes, 1,4-butanedial, 1,5-pentanedial, and 1,6-hexanedial, were found in both the particle and gas phases. Of these, an authentic standard was available only for 1,5-pentanedial; the two others were tentatively identified by comparing their mass spectra with that of 1,5-pentanedial. The EI spectra give compound specific information, i.e., for carbonyl compounds a strong peak at m/z M − 197. The spectra of the compounds identified as 1,4-butanedial and 1,6-hexanedial showed prominent peaks at m/z 279 and 307, respectively, which are −14 and +14 mass units ($-CH_2-$ group) compared to the M − 197 peak of 1,5-pentanedial. In addition, the CI spectra showed the molecular ion peaks (M + 1) of the two compounds (i.e., m/z 477 for the 1,4-butanedial derivative and m/z *505* for the 1,6-hexanedial derivative). The retention time supports the identification, i.e., 0.98 min earlier than that of 1,5-pentanedial for 1,4-butanedial and 0.9 min later for 1,6-hexanedial. 1,5-Pentanedial was quantified with compound- specific ions, whereas 1,4-butanedial and 1,6-hexanedial were quantified using the carbonyl specific m/z 181 (see Table 4).

Three oxoalkanoic acids, 4-oxobutanoic acid, 5-oxopentanoic acid, and 6-oxo hexanoic acid, were identified in both the gas and particle phases. An authentic standard was available only for 4-oxobutanoic acid; however, the two other compounds could be identified, similar to the dialdehydes, by comparing their mass spectra with that of 4-oxobutanoic acid. Molecular peaks as well as characteristic fragments were found. Again the M − 197 fragments typical for carbonyls

TABLE 4. Chemical Compounds Used as Standards or Surrogates for Quantification

compds found in samples	standard or surrogates	quantification ions	retention time [min]	density [g/cm^3]	surrogate for density
oxalic acid	oxalic acid	219	8.533	1.9	
malonic acid	malonic acid	233	9.931	1.619	
succinic acid	succinic acid	247	11.082	1.572	
glutaric acid	glutaric acid	261	12.348	1.424	
adipic acid	adipic acid	275	13.748	1.36	
4-hydroxy-1-butanal	4-oxobutanic acid	73,75,181	14.983	0.817	butanal
hydroxypentanoic acid	3-OH-3-me-glutaric acid	73,75	11.390	0.9391	pentanoic acid
hydroxyglutaric acid	3-OH-3-me-glutaric acid	73,75	14.716	1.424	glutaric acid
hydroxyadipic acid	3-OH-3-me-glutaric acid	73,75	15.817	1.36	adipic acid
4-oxobutanoic acid	4-oxobutanoic acid	354,188,172	16.014		
5-oxopentanoic acid	4-oxopentanoic acid	73+75+181	17.049	0.9391	pentanoic acid
6-oxohexanoic acid	5-oxohexanoic acid	73+75+181	18.149	0.93	
1,4-butanedial	1,5-pentanedial	181	20.284	0.817	butanal
1,5-pentanedial	1,5-pentanedial	309,293	21.166	0.8095	pentanal
1,6-hexanedial	1,5-pentanedial	181	21.149	0.8095	hexanal
pentanal	pentanal	181	11.698	0.8095	

were prominent for 5-oxopentanoic acid and 6-oxohexanoic acid at $m/z + 14$ and $m/z + 28$, compared to the spectrum of 4-oxobutanoic acid. Fragments also characteristic for the carboxyl group (i.e., M − 15 and M − 89) were found in both compounds. Again, the retention time supports the identification as 5-oxopentanoic acid and 6-oxohexanoic acid (see Table 4). For quantification, m/z 73+75+181 using the surrogates 4-oxopentanoic acid and 5-oxohexanoic acid, respectively, were used for 5-oxopentanoic acid and 6-oxohexanoic acid. 4-Oxobutanoic acid was quantified with the compound-specific ions.

All five dicarboxylic acids identified, oxalic acid, malonic acid, succinic acid, glutaric acid, and adipic acid, were verified with authentic standards and were quantified with compound-specific ions (Table 4).

Four different compounds with a hydroxyl functional group were tentatively identified: hydroxypentanoic acid, hydroxyglutartic acid, hydroxyadipic acid, and 4-hydroxy-1-butanal. The compound occurring in the chromatogram at 11.04 min has been tentatively identified as hydroxypentanoic acid. In the CI spectrum the molecular ion, m/z 262, was visible as well as the adduct M + 73, which is typical for compounds with a derivatized carboxyl or hydroxyl group. In the EI mode the spectrum showed a strong peak at mass m/z 247, which is the typical M − 15 fragment observed for all carboxyl and hydroxyl compounds, assuming m/z 262 is the molecular ion as found under CI conditions. This molecular mass can be attributed theoretically to three different compounds in this context, i.e., succinic acid, hexanediol, and hydroxypentanoic acid. Standards were available for the first two compounds; however, their retention times did not match with the peak at 11.04 min. Glutaric acid was used as a surrogate to quantify the amounts of hydroxypentanoic acid using the ions m/z 73 and 75.

Hydroxyglutaric acid was similarly identified by rationalizing the mass spectrum occurring at 14.7 min in the chromatogram. The CI spectrum showed again a prominent peak at m/z M + 73 and at m/z M + l, although the latter was rather weak. In the El mode spectrum the corresponding fragments, m/z 349 (M − 15), m/z 247 (M − 117), and m/z 147, were found. 3-Hydroxy-3-methylglutaric acid was used as a surrogate to quantify the amounts of hydroxyglutaric acid using the ions m/z 73+75.

The peak at 15.90 min retention time showed a similar spectrum to that for hydroxyglutaric acid, except that all relevant mass fragments were shifted by 14 mass units toward higher masses; mass unit 14 is typically assigned to a $-CH_2-$ group, and thus this compound was tentatively identified as hydroxyadipic acid and quantified with 3-hydroxy-3-methylglutaric acid as surrogate.

The peak at 15.05 min was characterized by the presence of m/z 181 and m/z 73+75, indicating that the compound has a carbonyl as well as a carboxyl or hydroxyl group. The CI spectrum shows weak peaks at m/z 356 and m/z 340 and the base peak at m/z 266, which were assigned to M + 1, M − 15, and M − 89, respectively, of 4-hydroxy-1-butanal. In the EI spectrum the fragment m/z 158 (M − 197) strengthened the identification of this peak as 4-hydroxy-1-butanal. For quantification, the surrogate 4-oxobutanoic acid was used. Pentanal, found only in the gas phase, was identified and quantified with an authentic standard.

At a retention time of 15.96 min, 5-oxopentyl formate was tentatively identified. In the CI spectrum the molecule ion (m/z 325) was prominent with 16% relative intensity. The main peak in the CI spectrum was m/z 280 (M − 45), corresponding to the loss of formate from the molecule. In addition, the fragment M − 197, prominent in the CI spectrum, and m/z 181, especially strong in the EI spectrum, both typical for carbonyls, supported the identification. 5-Oxopentyl formate was the only compound identified that was not quantified, since no appropriate standard was available.

Quantification of Reaction Products. The molecular yield of cyclohexene-O_3 reaction products in the gas and particulate phases and the total yield are given in Table 5. The largest single yield was measured for pentanal at 17%. This agrees with that reported by Grosjean et al. (*3*) of 16% and by Hatakeyama et al. (*1*) of 17%. The two other groups of compounds with high molar yields are dicarboxylic acids and oxocarboxylic acids, at about 22% and 16%, respectively. Among the dicarboxylic acids, oxalic acid, malonic acid, and glutaric acid are the most abundant, whereas succinic acid and adipic acid were found in smaller quantities. All three oxocarboxylic acids (4-oxobutanoic acid, 5-oxopentanoic acid, 6-oxohexanoic acid) were formed in about equal amounts (4−7%). Dialdehydes and hydroxylated compounds were produced in only minor amounts. The overall average carbon yield, both gas and particle phase, of the experiments was about 47% (see Table 5), that is, only about one-half of the carbon atoms originally present in the cyclohexene were recovered in the 16 compounds quantified in this study. Much of the missing carbon can likely be attributed to volatile products that could not be identified with the technique used in this study. For example, Hatakeyama et al. (*1*) found significant amounts of CO, CO_2, and HCOOH. If one assumes that for all compounds with fewer than six carbon atoms corresponding compounds with one or two carbon atoms were produced, the carbon balance increases to about 62%.

The average distribution of aerosol composition is shown in Figure 3. Total particle mass was calculated from the

TABLE 5. Average Molar Yield (%) of All Quantified Compounds

	total molar yield		gas-phase molar yield		aerosol molar yield		
compd name	av	std dev	av	std dev	av	std dev	carbon yield av
oxalic acid	6.16	3.15	4.83	2.69	1.33	0.35	2.04
malonic acid	6.88	3.68	6.25	3.46	0.63	0.23	3.41
succinic acid	0.63	0.34	0.49	0.31	0.14	0.04	0.41
glutaric acid	5.89	3.37	5.20	3.36	0.69	0.92	4.87
adipic acid	2.20	1.10	1.46	0.82	0.74	1.08	2.18
4-hydroxybutanal	2.60	2.54	1.96	2.08	0.64	0.31	1.58
hydroxypentanoic acid	1.02	0.62	0.84	0.56	0.18	0.20	0.73
hydroxyglutaric acid	2.33	1.51	0.34	0.24	1.99	2.56	1.46
hydroxyadipic acid	1.19	0.26	0.23	0.09	0.97	0.48	1.27
4-oxobutanoic acid	6.90	4.62	6.48	4.59	0.42	0.25	4.56
5-oxopentanoic acid	4.52	3.09	4.13	3.07	0.39	0.23	3.73
6-oxohexanoic acid	4.16	3.30	3.77	3.34	0.39	0.22	4.13
1,4-butandial	0.53	0.41	0.45	0.39	0.08	0.06	0.30
1,5-pentanedial	0.44	0.20	0.40	0.18	0.04	0.03	0.36
1,6-hexanedial	1.64	1.15	1.62	1.15	0.03	0.02	1.72
pentanal	17.05	9.39	17.05	9.39			14.1
sum	64.14		55.48		8.66		46.86
							61.9[a]

[a] Percent recovery if small C1, C2 compounds are included (see text).

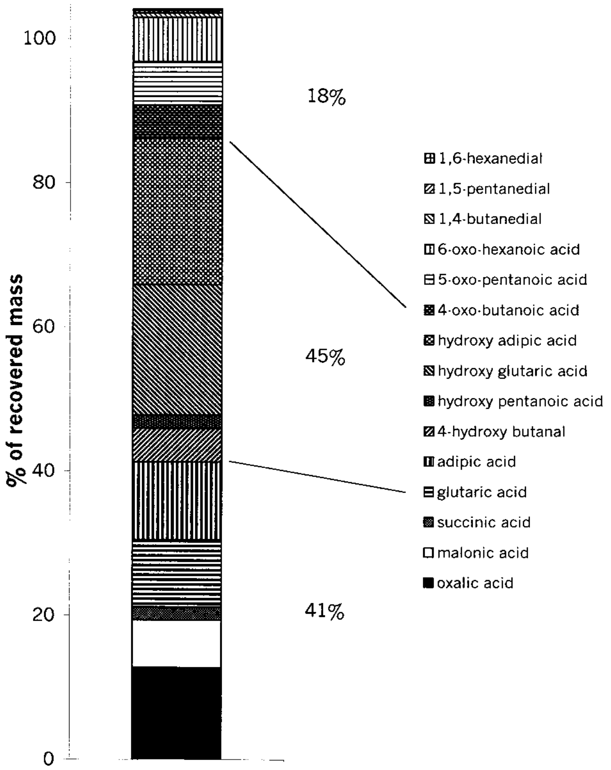


FIGURE 3. Molecular distribution of the particle composition. 104% of the particle mass could be resolved on a molecular level assuming a weighted particle density of 1.4 g cm^{-3}.

measured increase of the particle diameter using a density of the organic mass of $\rho = 1.4$ g cm^{-3}, which is the weighted average of the densities of the individual compounds listed in Table 5. Dicarboxylic acids contribute about 41% of the aerosol mass. The two hydroxylated dicarboxylic acids, hydroxyglutaric acid and hydroxyadipic acid, contribute about one-third to the aerosol mass (38%). Although their overall molar reaction yields are rather small (3.5%), they contribute significantly to the particle mass because of their low vapor pressures. About 17% of the particle mass consists of oxocarboxylic acids; dialdehydes account for only a small amount, about 1.1%.

By summing all the individual compounds, the average total aerosol mass was 104% of the volume calculated from the DMA size measurements based on an estimated aerosol density of 1.4 g cm^{-3}. This agreement between the two independent methods indicates that the entire aerosol mass has been accounted for on a molecular level, subject to uncertainties inherent in the chemical analysis and the assumed particle density.

Cyclohexene-Ozone Reaction Mechanism. The initial reaction between cyclohexene and ozone is the well-established addition of ozone to the double bond leading to the energy-rich Criegee biradical (Figure 4a) (*10*). Loss of CO_2 from the Criegee biradical leads to the formation of pentanal (b), the most abundant identified reaction product (Figure 4b). The Criegee biradical can also react with water and by subsequent loss of H_2O_2 and H_2O lead to 1,6-hexanedial (c) and 6-oxohexanoic acid (d), respectively. Adipic acid (e) might be formed by oxidation of 6-oxohexanoic acid, although an explicit mechanism for this reaction is not obvious (Figure 4c). Similarly, we speculate that other acid products, h, i, n, o, p, q, are formed from their corresponding aldehyde precursors.

Intramolecular isomerization of the Criegee biradical leads to an excited intermediate (f) and by subsequent loss of CH_2O can lead to 1,5-pentanedial (g), which is oxidized to 4-oxo-pentanoic acid (h) and further to glutaric acid (i) (Figure 4d). The intermediate (f), however, can also lead to the C_4 compounds identified in this study as outlined in Figure 4e. This reaction chain involves the cleavage of a C−C bond of the intermediate alkoxy radical (j), which leads either to a C_4 alkyl radical (k) or the C_5 compound 1,5-pentanedial (g). After reaction with O_2 and H_2O the alkyl radical (k) is converted to a second alkoxy radical (l), which can react to 1,4-butanedial (m) and by further oxidation to 4-oxobutanoic acid (n) and succinic acid (o). Another pathway the intermediate alkoxy radical (1) can undergo is a cleavage and subsequent reaction to malonic (p) and oxalic acid (q) (see Figure 4f).

A possible reaction mechanism for the formation of hydroxyadipic acid is shown in Figure 4g. After an initial H abstraction from adipic acid, the reactions with O_2 and H_2O lead to the formation of hydroxyadipic acid. The path of formation of hydroxyglutaric acid is thought to be equivalent to that leading to hydroxyadipic acid. CO was present in the reaction chamber, which should have scavenged about 95% of the OH radicals generated in the cyclohexene-O_3 reaction.

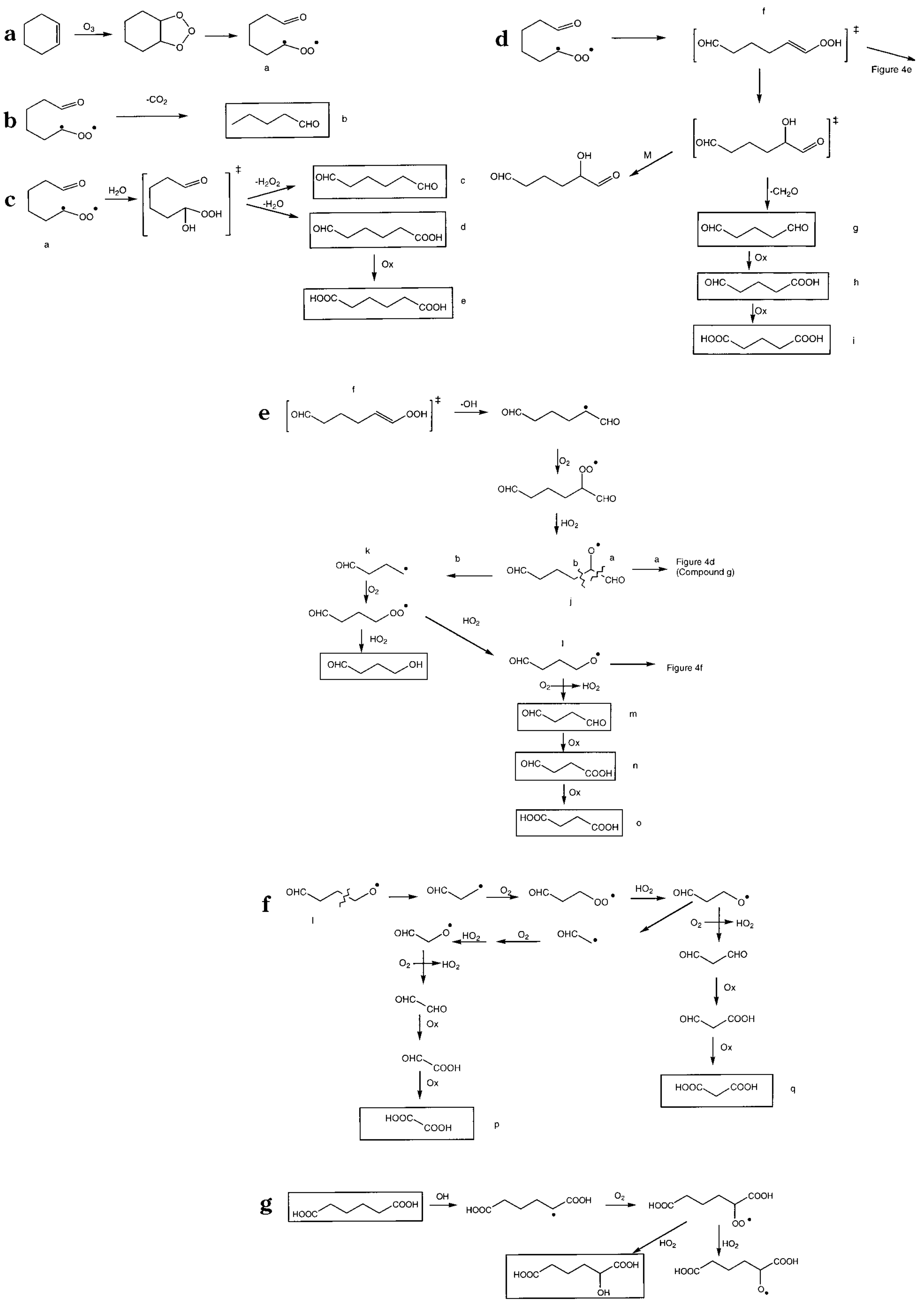


FIGURE 4. (a)−(g) Proposed reaction mechanism of the cyclohexene-ozone reaction leading to the products observed in this study. For details see text. The combined mass of all individual compounds is 104% of the mass determined from DMA measurement, based on an assumed aerosol density of 1.4 g cm^{-3}.

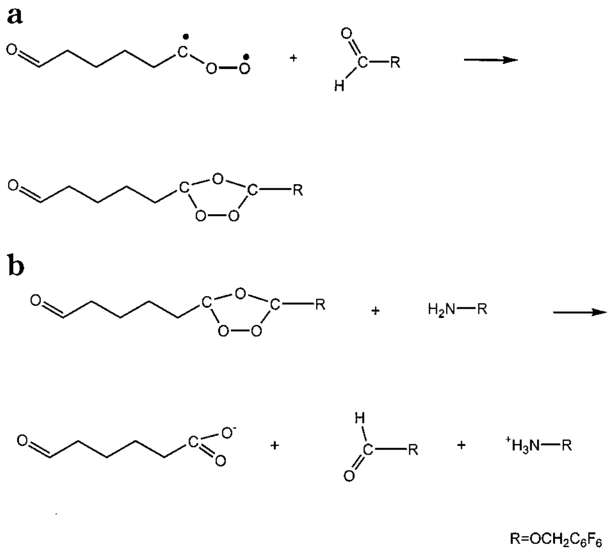


FIGURE 5. (a) The Criegee biradical can react with aldehydes to a second ozonide. (b) Ozonides, like the reaction product of (a), might react with the derivatization agent PFBHA, a primary amine, to form an aldehyde and an acid.

It is not clear whether the formation of hydroxyglutaric acid and hydroxyadipic acid (molar yields: 1.6 and 0.9%, respectively) was a result of unscavenged OH radicals or whether another reaction mechanism is responsible for the formation of these two compounds.

The Criegee biradical can undergo reaction with aldehydes to produce ozonides (*11, 12*) (Figure 5a). Since different aldehydes are present as reaction products, formation of ozonides is likely. No ozonides were detected; however, a possible reason might be their decomposition during sample treatment. PFBHA is a primary amine that can react with ozonides leading to an aldehyde and an acid (*13*) (Figure 5b). The occurrence of the relatively high vapor pressure particle-phase aldehydes and acids might actually be a result of ozonide decomposition products. While another possibility could be thermal decomposition of ozonides during the Soxhlet extraction of the filter samples, which was performed at about 70 °C, at temperatures below 100 °C the decomposition reactions are probably too slow to contribute to a significant loss for the ozonides (*14*). We do not exclude the possibility that products of relatively high volatility, such as hexanedial and pentanedial, were present in the aerosol phase. Even if the presence of these relatively high vapor pressure compounds in the aerosol phase resulted from experimental artifacts, they represent only about 4% of the aerosol mass and therefore do not compromise the general results of this study.

Acknowledgments

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