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Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone

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A series of smog chamber experiments have been conducted in which five cyclic monoterpenes were oxidized by ozone. The evolved secondary aerosol was analyzed by GC-MS and HPLC-MS for nonvolatile polar oxidation products with emphasis on the identification of carboxylic acids. Three classes of compounds were determined at concentration levels corresponding to low percentage molar yields: i.e. dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids. Carboxylic acids are highly polar and have lower vapor pressures than their corresponding aldehydes and may thus play an important role in secondary organic aerosol formation processes. The most abundant carboxylic acids were the following: *cis*-pinic acid **AB1** (*cis*-3-carboxy-2,2-dimethylcyclobutylethanoic acid) from α- and β-pinene; *cis*-pinonic acid **A3** (*cis*-3-acetyl-2,2-dimethylcyclobutylethanoic acid) and *cis*-10-hydroxypinonic acid **AB6** (*cis*-2,2-dimethyl-3-hydroxyacetylcyclobutylethanoic acid) from α-pinene and β-pinene; *cis*-3-caric acid **C1** (*cis*-2,2-dimethyl-1,3-cyclopropyldiethanoic acid), *cis*-3-caronic acid **C3** (2,2-dimethyl-3-(2-oxopropyl)cyclopropanylethanoic acid), and *cis*-10-hydroxy-3-caronic acid **C6** (*cis*-2,2-dimethyl-3-(hydroxy-2-oxopropyl)cyclopropanylethanoic acid) from 3-carene; *cis*-sabinic acid **S1** (*cis*-2-carboxy-1-isopropylcyclopropylethanoic acid) from sabinene; limonic acid **L1** (3-isopropenylhexanedioic acid), limononic acid **L3** (3-isopropenyl-6-oxo-heptanoic acid), 7-hydroxylimononic acid **L6** (3-isopropenyl-7-hydroxy-6-oxoheptanoic acid), and 7-hydroxylimononic acid **L6′** (7-hydroxy-3-isopropenyl-6-oxoheptanoic acid) from limonene.

Introduction

Smog chamber experiments carried out over the past 2 decades have identified secondary organic aerosol (SOA) from gas-phase oxidation of volatile organic compounds (VOC) as a potentially important contributor to the atmospheric burden of particulate matter (*1−11*). Although observations of blue haze in the atmosphere deriving from compounds emitted by trees date back to 1960 (*12*), organic aerosol research has mainly been focused on anthropogenic VOC and their SOA forming potential with relevance to urban air quality. The growing interest about biogenically emitted compounds such as terpenes, estimated on a global scale to amount to 120−480 Tg y^{-1} (*13, 14*), has triggered investigations of the SOA forming potential of these compounds. The first results indicate that biogeochemical sources of SOA may play an important role in atmospheric chemistry (*15−17*).

Although very little is known about the mechanism for the photochemical gas-to-particle conversion of terpenes it is conceivable that the formation of oxidation products with considerably lower vapor pressures than the parent compounds plays an important role. The main products of gas-phase reactions of terpenes with O_3, OH, or NO_3 are carbonyl compounds, which are produced in molar yields up to 60% but only found in low concentrations in SOA (*1, 5, 7−9, 18−20*). Carbonyls generally possess relatively high vapor pressures and cannot reach supersaturation to nucleate or condense under the experimental conditions used. This applies even for high molecular weight (C_{10}) ketoaldehydes, such as e.g. the main oxidation product of α-pinene and of 3-carene (*21*). Therefore, to explain the particle burst in most SOA experiments attention has been turned to multifunctional secondary products such as carboxylic acids, oxocarboxylic acids, hydroxyketones, hydroxycarboxylic acids, diols, and dicarboxylic acids with stronger intermolecular forces and much lower vapor pressures.

Pinonic acid **A3**, a ketocarboxylic acid (3-acetyl-2,2-dimethylcyclobutylethanoic acid) is a well-known minor oxidation product of α-pinene, found both in the gas-phase and the particle phase (*1, 7, 10, 11, 18−21*). Pinic acid **AB1**, a dicarboxylic acid (3-carboxy-2,2-dimethylcyclobutylethanoic acid), was identified for the first time during smog chamber experiments in 1997 in SOA from α-pinene/O_3 (*22, 23*) and β-pinene/O_3 (*22*) together with a decarboxylated analogue, norpinic acid **AB2** (3-carboxy-2,2-dimethylcyclobutylmethanoic acid). The reported yields of these compounds (0.1−3%) can only account for a small proportion of the evolved aerosol mass. By the use of various chemical derivatization approaches combined with gas chromatography−mass spectrometry (*24−26*) and gas chromatography-Fourier transform infrared spectroscopy (*25*) to obtain information on molecular mass and functional groups, recent investigations have steadily increased the number of identified nonvolatile terpene oxidation products in SOA from α-pinene (*24−26*), β-pinene (*26*), 3-carene (*24, 26*), sabinene (*26*), and limonene (*26*). Nevertheless, a large proportion of the aerosol mass still cannot be accounted for.

In this study characterization of the particle phase reaction products from the reaction of the cyclic monoterpenes α-pinene, β-pinene, 3-carene, sabinene, and limonene with ozone was undertaken. A newly developed analytical method was employed based on liquid chromatography interfaced with tandem mass spectrometry (LC-MS^n) using electrospray ionization and atmospheric pressure chemical ionization (*27*). The aim was primarily to identify new products in the particle phase and to confirm previous tentatively identified products, but attempts were also made to obtain quantitative information on the particle composition. The choice of terpenes was based upon their high emission rates from vegetation and their proven SOA forming potential (*11, 17*).

Experimental Section

Smog Chamber Experiments. The experiments were carried out in 600−1200 L Teflon (PTFE) reaction chambers. Individual terpenes were oxidized by ozone and the evolved SOA was sampled and analyzed. The investigated compounds were the cyclic monoterpenes (+)-α-pinene, (+)-β-pinene, (+)-3-carene, (−)-limonene, and (+)-sabinene (Figure 1) used

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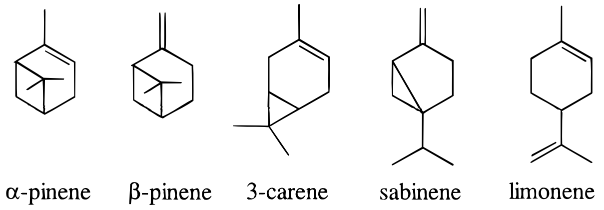

FIGURE 1. Terpenes used in the present investigation. In the text the identified ozonolysis products from each terpene are nominated with a letter (A, B, C, S, L, for α-pinene, β-pinene, 3-*c*arene, *s*abinene, and *l*imonene, respectively) and a number in bold.

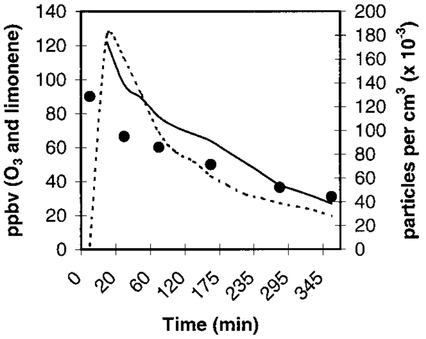

FIGURE 2. Typical evolution of a smog chamber experiment. Limonene (90 ppbv) + O_3 (122 ppbv) + methylcyclohexane (1.5 ppmv) as OH scavenger. Black bullets = limonene mixing ratio; dotted line = particle number concentration; solid line = ozone mixing ratio.

in initial mixing ratios from 80 ppbV to 13 ppmV. All terpenes were obtained from Fluka (Milan, Italy). Stereochemical characterization of ozonolysis products of terpenes has recently been published by Griesbaum et al. (*28*). In the present study pure stereoisomers terpenes were used merely due to the fact that these could be obtained in a higher chemical purity than racemic terpenes. Pinic acid **AB1** and pinonic acid **A3** were obtained from Aldrich (Milan, Italy); pinonaldehyde **A7** and limononaldehyde **L7** were synthesized in the laboratory (*29*). All compounds including terpenes, solvents, and reagents were used in 99% purity. It is important to note that, although the initial terpene concentrations are orders of magnitudes above ambient levels over natural vegetation (*13, 14, 28*), the ozone and hydroxyl radical chemistry occurring in the chambers is largely independent of concentration (*30*). Hence, the products formed and the mechanism of formation are expected to be valid for ambient conditions. However, since the reactant concentrations will influence the relative importance of competing reactions (e.g. reactions of organic species with O_2 and H_2O compared to reactions with other organic species), the reaction yields determined in this investigation do not necessarily give accurate estimates of ambient yields.

The experiments were carried out in purified air at 740 ± 5 Torr, 298 ± 5 K, and at medium humidity (40−55% RH). The desired terpene mixing ratios were obtained by direct injection of a few microliters of the liquid terpene into the reaction chamber (high levels) or into a dilution cell (low levels).

Ozone was prepared by silent discharge and afterward introduced into the reaction chamber. To address the importance of secondary OH evolved during ozonolysis of terpenes the experiments were carried out with and without addition of cyclohexane as OH scavenger (*31*). SOA was monitored by a condensation nucleus counter. Experimental details are summarized in Table 1.

Sample Collection. SOA was collected on PTFE filters (0.5 μm Fluoropore membranes from Millipore, Rome, Italy). Terpenes are known to react rapidly with ozone not only in the gas-phase but also in the adsorbed state during sampling (*32*) thereby forming significant yields of artifact reaction products on the adsorbent (*33, 34*). Ozone scrubbers have been developed for sampling of reactive products in the gas-phase. However, these tend to discriminate toward large diameter particles and are therefore not ideal for SOA sampling (*34*). To minimize artifacts from ozone during sampling, a simple approach has been used to draw samples at the end of each experiment when only low concentrations of residual ozone was present, typically after 6 h. Possible artifacts from residual ozone at these concentrations were addressed in separate experiments by purging PTFE fiber filters impregnated with terpene with air containing ozone. No evidence of carboxylic acid formation was observed.

Terpenes are known to undergo rearrangement reactions on acidic surfaces (*35*). Thus, the use of glass or quartz fiber material was avoided. Air, with its content of SOA, was drawn from the reaction chambers at a rate of 1−2.5 L min^{-1} through PTFE filters (2.5 cm in diameter with a 0.5 μm pore size) for the duration of 30−200 min. The sampling volume corresponded to 40−500 NL. A minimum of two samples was collected for each experiment. One filter was extracted and analyzed immediately by gas chromatography-MS (GC-MS). The other filters were stored at −20 °C in 10 mL sealed glass vials for later analysis by HPLC-MS^n. The filter samplers were cleaned by sonication in distilled water followed by sonication in methanol between experiments. Tests with the PTFE filters proved the absence of particle breakthrough. However, it cannot be excluded that artifacts in the particle sampling may have occurred due to size dependent charge distribution or sedimentation after 6 h in the smog chambers.

Extraction and Analysis. A sample preparation protocol directed toward GC-MS eletron impact (EI) and chemical ionization (CI) analysis of carboxylic acids was adapted from Christoffersen et al. (*22*). The PTFE filters were sonicated with 7 mL of dichloromethane at room temperature, the filters were removed, the solvent was evaporated under a gentle stream of nitrogen, and the residues were treated with 300 μL 10% BF_3−methanol at 50 °C for 30 min in order to esterify the organic acids. The solution was cooled, 300 μL distilled water was added, and the esters were extracted with 2 mL of pentane containing 2 ng μL^{-1} bornyl acetate as internal reference compound. A second extraction step with methanol−water (1:1) was applied occasionally to look for highly polar compounds such as e.g. tricarboxylic acids. No such compounds were found. Stored filters were analyzed with a newly developed HPLC-MS^n method using atmospheric pressure chemical ionization (APCI) and pneumatically assisted electrospray chemical ionization (ESI), which have proved efficient for polar terpene oxidation products (*27*). Detailed descriptions of the mass spectrometric methods are given in the Supporting Information.

Monitoring of the terpene concentrations was done by drawing air samples at the beginning, the end, and occasionally during the experiments onto Tenax tubes through ozone scrubbers (*33, 34*). The Tenax tubes were later analyzed by thermal desorption GC-MS according to Calogirou et al. (*33*).

Results and Discussion

A typical evolution of a smog chamber experiment is shown in Figure 2. Shortly after contact of ozone with terpene a particle burst of SOA occurs, which reaches a maximum in number concentration after a few minutes. In the ensuing period ozone and terpene are consumed, but coagulation of already existing particles proceeds more rapidly than the formation of new particles, and as a result, decay curves are obtained. If wall losses are minor, the mass concentration of SOA will increase during the decay of the reactants. To

TABLE 1. Experimental Conditions for Smog Chamber Experiments and Resulting Yields of Reaction Products in Organic Aerosol

terpene	$[HC]_0 -$ $[HC]_{end}$, ppmV	$[O_3]_0 -$ $[O_3]_{end}$, ppmV	[MCH], ppm	particles max., cm^{-3}	molar yield[a] of reaction products detected in organic aerosol, %						
					pinic	norpinic	pinonic	norpinonic[d]	OH-pinonic[d]	pinonaldehyde/OH-pinonaldehyde	sum
α-pinene	1.8–0.29	0.91–0.005	0	18300	1.9	0.09	2.1	0.32	1.7	2.1/0.51	8.7
	1.9–0.28	0.82–0.005	16	17200	1.4	0.04	1.5	0.19	0.86	1.9/0.32	6.2
					3-caric	nor-3-caric	3-caronic	nor-3-caronic	OH-3-caric[d]	3-caronaldehyde/OH-3-caronaldehyde	sum
3-carene	6.5–6.0	0.64–0.005	0	na[b]	1.6	0.13	0.91	0.01	na[b]	na[b]	2.6[e]
	0.103–0.029	0.24–0.036	0	41000	2.9	0.09	4.8	0.03	5.1	3.7/0.64	17
	0.105–0.027	0.13–0.064	1.3	40500	0.67	trace	0.21	trace	0.13	1.4/0.17	2.6
					pinic	norpinic	pinonic	norpinonic[d]	OH-pinonic[d]	nopinone/OH-pina ketone[d]	sum
β-pinene	1.9–1.7	0.89–0.020	0	23700	3.9	0.18	0	trace	na[b]	1.1/na[b]	5.2[e]
	0.046–0.014	0.11–0.044	0	13000	1.2	0.11	0	0	0.14	0.19/0.34	2.0
	0.042–0.016	0.10–0.059	1.6	2000	0.46	0.01	0	0	0.05	0.02/0.05	0.6
					sabinic	norsabinic	pinic			sabina ketone/OH-sabina ketone[d]	sum
sabinene	2.0–1.0	0.75–0.005	20	na[b]	2.7	0.08	0.09			1.3/na[b]	4.2
	1.1–0.26	0.49–0.009	0	38300	1.1	0.03	1.4			0.80/0.31	3.7
	0.40–0.10	0.5[c]- 0.009	0	13500	0.26	trace	0.64			0.08/0.03	1.0
	0.51–0.08	0.5[c]–0.084	1.6	8700	0.20	trace	0.22			0.05/0.03	0.5
					limonic/keto-limonic	norlimonic	limononic/keto-limononic	nor-limononic[d]	OH-limononic[d]/OH-keto-limononic[d]	limononaldehyde/OH-limononaldehyde	sum
limonene	13.3–9.5	3.8–0.130	0	na[b]	0.06/0.01	0.003	0.22/trace	0.01	0.36/0.03	0.60/0.09	1.4
	3.6–1.9	1.8–0.154	0	140000	0.36/0.04	0.01	0.64/0.01	0.09	0.90/0.08	0.91/0.08	3.1
	0.090–0.033	0.12–0.064	0	40000	0.91/0.04	0.004	1.3/trace	0.19	na[b]	na[b]	2.3[e]
	0.080–0.002	0.14–0.094	6.5	18000	0.30/0.02	trace	0.23/trace	0.07	na[b]	na[b]	0.6[e]

[a] The propagated estimated error on yields amounts to less than a factor 2. [b] na = not analyzed. [c] Malfunctioning ozone analyzer, the value is estimated based on elapsed time with UV light on. [d] Sum of all isomers. [e] Not all compound classes were analyzed. MCH = methyl-cyclohexane, used as OH radical scavenger. OH as prefix denominates a hydroxy derivate.

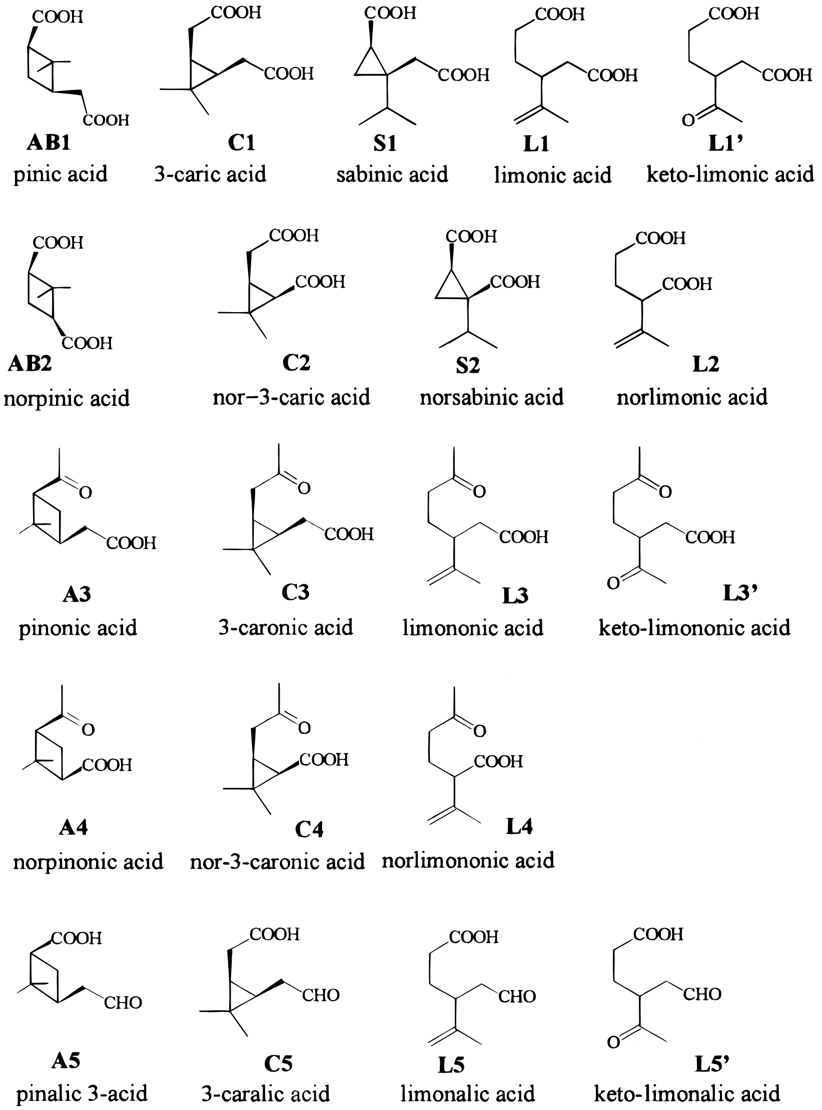

FIGURE 3. Dicarboxylic acids and oxocarboxylic acids in secondary organic aerosol formed by gas-phase reactions between terpene and ozone.

sample as much particle mass as possible SOA was collected at the end each experiment.

In the following, data are first presented to support tentative identifications of nonvolatile polar oxidation product in the SOA extracts. Second, semiquantitative results of the analyses are discussed. Mass spectra of a large number of oxidation products in SOA have been recorded during this study. Examples of representative mass spectra are shown in the Supporting Information together with a detailed discussion of their interpretation. Three classes of carboxylic acids were determined (dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids) together with the well-known classes of ketones and ketoaldehydes. The proposed structures of individual compounds are shown in Figures 3 and 4 together with shorthand names according to Larsen et al. (*37*). For clarity, the corresponding IUPAC names and a letter and a number in bold (Figure 1) are given in the text first time a new reaction product is mentioned.

Dicarboxylic Acids. For all terpenes the HPLC-MS^n analysis of the SOA extract gave chromatograms with a few major peaks and a number of minor peaks (Figure 5 and 6). For the major peaks it was possible to obtain high quality GC-EI-MS and GC-CI-MS spectra, which supported tentative structure assignments. The most abundant class of compounds was dicarboxylic acids. The proposed structures are *cis*-pinic acid **AB1** (*cis*-3-carboxy-2,2-dimethylcyclobutylethanoic acid) from α- and *β*-pinene; *cis*-3-caric acid **C1** (*cis*-2,2-dimethyl-1,3-cyclopropyldiethanoic acid) from 3-carene; *cis*-sabinic acid **S1** (2-carboxy-1-isopropylcyclopropylethanoic acid) from sabinene; and limonic acid **L1** (3-isopropenylhexanedioic acid) and ketolimonic acid **L1′** (3-acetylhexanedioic acid) from limonene.

By comparing mass spectral data and retention times with those of an authentic standard, *cis*-pinic acid **AB1** was unambiguously identified as a main oxidation product in SOA not only from α-pinene and *β*-pinene but surprisingly also from sabinene. Even in SOA from 3-carene minor yields of *cis*-pinic acid **AB1** were found. A number of control experiments including blank runs with newly prepared PTFE reaction chambers and new batches of terpene standards excluded that cross-contamination could be the reason for these findings. For more than a century, terpenes have been known to undergo (Wagner-Meerwein) rearrangements of their carbon skeleton either in solution or when adsorbed onto active surfaces (*35, 38*−*39*). The more strain there is in the terpene structure the stronger the tendency is to rearrange (*39*−*41*). A recent example of this has been given by Coeur et al. who observed a significant transformation (72%) of sabinene into other terpenes after adsorption to steel and Tenax surfaces (*42*). Likewise it has been demonstrated that

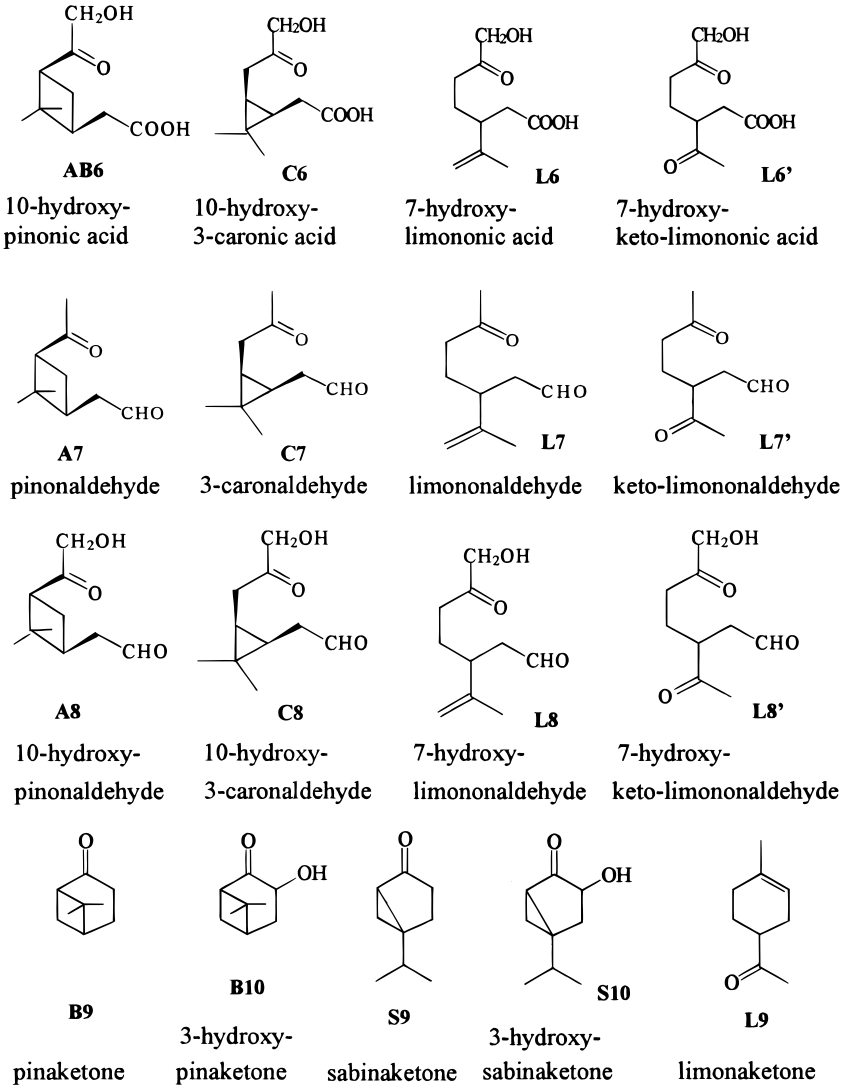

FIGURE 4. Hydroxycarboxylic acids, ketoaldehydes, hydroxyketoaldehydes, ketones, and hydroxyketones in secondary organic aerosol formed by gas-phase reactions between terpene and ozone.

intermediate (radical) reaction products of terpenes after an OH attack can undergo skeleton rearrangements (*20, 43, 44*), and it is not unlikely that also the exited Criegee biradical intermediate products of terpenes after an O_3 attack may undergo rearrangements. Hence, the finding of dicarboxylic acids in SOA with carbon skeletons that have lost most of their resemblance with the precursor terpene—surprising as it may be—is perfectly explainable. The four-member ring in the structure of pinic acid **AB1** is considerably less strained than the three-member rings in the structure of sabinic acid **S1** and 3-caric acid **C1** and thus, during rearrangement reactions, pinic acid **AB1** is energetically favored over the latter two dicarboxylic acids. The formation of pinic acid **AB1** in SOA from sabinene and 3-carene has also been observed by others (*45*).

Based on GC-EI and GC-CI mass spectral data 3-caric acid **C1**, sabinic acid **S1**, and limonic acid **L1** have previously been tentatively identified in SOA from 3-carene, sabinene, and limonene by Glasius et al. (*26*) using esterification with BF_3/MeOH. These dicarboxylic acids have also been reported by Yu et al. (*24, 45*) using derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyamine and *N,O*-bis(trimethylsilyl)trifluoroactamide. Both methods have their advantages. A high degree of fragmentation with detailed structural information is obtained by EI analysis of methyl ester derivatives. However, the introduction of methyl groups into the analytes may disconcert their identification by diminishing spectral differences of methylated SOA components and nonmethylated components containing an extra $-CH_2-$ group in its molecular structure. By introducing the larger groups *O*-(2,3,4,5,6-pentafluorobenzyl)oxime and trimethylsilyl into the analytes such ambiguity is avoided. Yet, the large groups adsorb most of the energy during the electron impact ionization, which results in considerably less fragmentation of the carbon skeleton. The use of both GC-MS after methylation of the SOA extracts and direct HPLC-MS^n analysis of the extracts, as in the present investigation, gave complementary information on the analytes and confirmed the previous tentative identification of 3-caric acid **C1**, sabinic acid **S1**, and limonic acid **L1**.

In addition to the C_9-dicarboxylic acid less abundant peaks were present in the chromatograms with mass spectral data also pointing to C_8-dicarboxylic acids. The proposed structures for these compounds (Figure 3) are *cis*-norpinic acid **AB2** (*cis*-3-carboxy-2,2-dimethylcyclobutylmethanoic acid) from α- and *β*-pinene, *cis*-nor-3-caric acid **C2** (3-carboxy-2,2-dimethylcyclopropanylethanoic acid) from 3-carene, *cis*-norsabinic acid **S2** (2-carboxy-1-isopropylcyclopropylmethanoic acid) from sabinene, and norlimonic acid **L2** (2-isopropenylpentanedioic acid) from limonene. A decarboxylated form of pinic acid **AB1**, namely norpinic acid **AB2**, has been tentatively identified in SOA from α-pinene/O_3 in

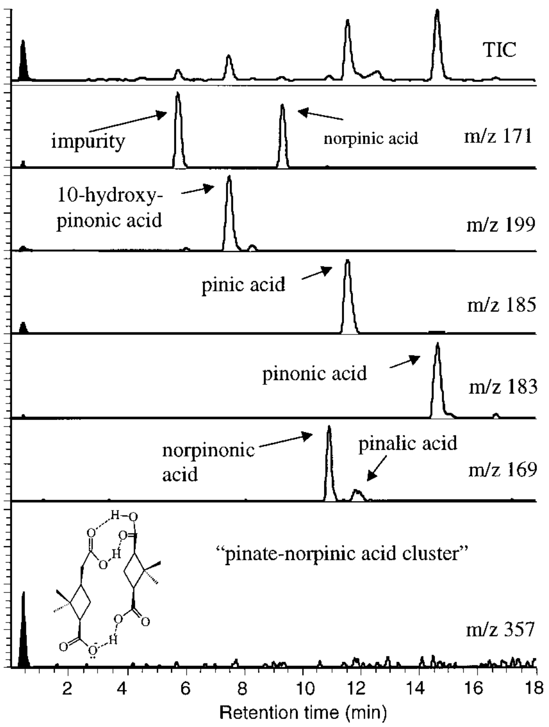

FIGURE 5. HPLC-ESI-MS chromatograms (TIC and extracted ions) of carboxylic acids in SOA from gas-phase oxidation of α-pinene with ozone. Black peaks at 30 s derive from postcolumn flow injection.

other studies based upon its online-APCI-MS^n spectral data, (*23*), HPLC-MS^n data (*27*), GC-MS (EI and CI) data (*25, 26*), and GC−FTIR data (*25*). Nor-3-caric acid **C2** and norsabinic acid **S2** are reported for the first time in the present study and by Yu et al. (*45*). Norlimonic acid **L2** is reported here for the first time.

Oxocarboxylic Acids. The second class of abundant compounds identified in SOA is the oxocarboxylic acids. The proposed structures of the tentatively identified compounds are shown in Figure 3 together with their shorthand names. The most abundant compounds are the C_{10}-ketocarboxylic acids. They are *cis*-pinonic acid **A3** (*cis*-3-acetyl-2,2-dimethylcyclobutylethanoic acid) from α-pinene; *cis*-3-caronic acid **C3** (2,2-dimethyl-3-(2-oxopropyl)cyclopropanylethanoic acid) from 3-carene; and limononic acid **L3** (3-isopropenyl-6-oxoheptanoic acid) and ketolimononic acid **L3′** (3-acetyl-6-oxoheptanoic acid) from limonene. The analogue C_9-ketocarboxylic acid were also present in the chromatograms (Figure 2). The intensities of the peaks were lower than those of the C_8-dicarboxylic acids. The compounds are tentatively identified as *cis*-norpinonic **A4** acid (*cis*-3-acetyl-2,2-dimethylcyclobutylmethanoic acid) from α-pinene, *cis*-nor-3-caronic acid **C4** (2,2-dimethyl-3-(2-oxopropyl)cyclopropanylmethanoic acid) from 3-carene, and norlimononic **L4** (2-isopropenyl-5-oxo-hexanoic acid) from limonene. C_9-ketocarboxylic acids are not very important contributors to the total aerosol load but are mentioned here for completeness.

Pinonic acid **A3** has been reported in SOA from smog chamber experiments by a number of investigators and most recently also in ambient aerosol over a forested area (*17*). Limononic acid **L3** and 3-caronic acid **C3** have been tentatively identified in SOA from limonene/O_3 (*26*) and 3-carene/O_3 (*24*). Norpinonic acid **A4** has been tentatively identified in SOA from α-pinene/O_3 by Hatakeyama et al. (*18*), Yu et al. (*24, 45*), and Jang and Kamens (*25*). Nor-3-caronic acid **C4** was tentatively identified in SOA from 3-carene/O_3 by Yu et al. (*24, 45*), whereas norlimononic acid **L4** is proposed here for the first time.

In SOA from α-pinene/O_3 small amounts of an isomeric form of norpinonic acid **A4** has previously been detected (*24, 27*). In Figure 5 the ESI(−)MS extracted ion chromatogram at *m*/*z* 169 shows traces of an isomeric form of norpinonic acid **A4**. A strong signal from neutral loss of H_2O by ESI(−)-MS^2 (and GC-CI) points to an aldo-acid rather than a keto-acid. Two possible structures fit the mass spectrometric data, namely pinalic 4-acid (2,2-dimethyl-3-formylcyclobutylethanoic acid) and pinalic 3-acid **A5** (2,2-dimethyl-3-formylmethylcyclobutylmethanoic acid). It is difficult to distinguish between these two isomers on the basis of mass spectral data alone. In Figure 3 we have shown the structure of pinalic 3-acid **A5** as representative of these two isomers. In SOA from 3-carene/O_3 and limonene/O_3 traces of similar aldocarboxylic acids were present. They are tentatively identified as 3-caralic acid **C5** (2,2-dimethyl-3-formylmethylcyclopropylethanoic acid), limonalic acid **L5** (3-formylmethyl-2-methylenylhexanoic acid), and ketolimonalic acid **L5′** (3-formylmethyl-2-oxohexanoic acid).

Hydroxyketocarboxylic Acids. C_{10}-hydroxyketocarboxylic acids were determined in SOA from the terpenes with an *endo*cyclic C=C double bond. They eluted as major peaks in the HPLC chromatograms 5−7 min before C_{10}-keto-carboxylic acid (Figures 4 and 5). In SOA from α-pinene and in a smaller amount from *β*-pinene *cis*-10-hydroxypinonic acid **AB6** (*cis*-2,2-dimethyl-3-hydroxyacetylcyclobutylethanoic acid) was identified by comparison of retention times and mass spectral data with those of a standard (*27*) produced by ozonolysis of myrtenol (10-hydroxy-α-pinene). The other representatives of this class of nonvolatile terpene oxidation products are tentatively identified as *cis*-10-hydroxy-3-caronic acid **C6** (*cis*-2,2-dimethyl-3-(hydroxy-2-oxopropyl)-cyclopropanylethanoic acid) from 3-carene and 7-hydroxylimononic acid **L6** (7-hydroxy-3-isopropenyl-6-oxoheptanoic acid) and 7-hydroxyketolimononic acid **L6′** (3-acetyl-7-hydroxy-6-oxoheptanoic acid) from limonene (Figure 4). The position of the hydroxy-group in the proposed structures for the hydroxyketocarboxylic acids from 3-carene and limonene is based upon similarities with 10-hydroxypinonic acid **AB6** in retention times and MS data. Other isomers may also be possible.

A mechanism for the α-pinene/O_3 reaction has been proposed by Yu et al. (*24*) to explain the formation of hydroxyketoaldehydes such as 10-hydroxypinonaldehyde **A8** and 2-hydroxypinonaldehyde in SOA from α-pinene/O_3 (*24*). According to this mechanism such compounds may arise by isomerization of Criegee radicals to form enehydroperoxides through *intra*molecular hydrogen migration followed by subsequent isomerization to hydroxyketoaldehydes. A further oxidation of these compounds would explain the formation of hydroxyketocarboxylic acids observed in the present study. Interestingly, also a number of minor peaks are present in the HPLC-MS chromatograms with mass spectral data corresponding to hydroxyketocarboxylic acids (Figures 4 and 5). They may correspond to 2-hydroxy-3-caronic acid (2,2-dimethyl-3-(2-oxopropyl)cyclopropanylhydroxyethanoic acid) and 2-hydroxylimononic acid (2-hydroxy-3-isopropenyl-6-oxoheptanoic acid) deriving from the O_3-mechanism suggested above or they may be other isomers deriving from mechanisms involving secondary OH radical. Traces of a compound assigned the structure of 10-hydroxypinonic acid **AB6** has also been reported in SOA from α-pinene/O_3 by Jang and Kamens (*25*) and Yu et al. (*45*).

Nonacidic Components of SOA. Ketones and ketoaldehydes are major gaseous products from the reaction of monoterpenes and ozone (*20*). Although the analytical procedures were not optimized for such compounds, HPLC-APCI(+)MS chromatograms and GC-MS chromatograms showed the presence of a number of compounds with mass spectral data corresponding to well-known main oxidation products of terpenes such as *cis*-pinonaldehyde **A7** (*cis*-3-acetyl-2,2-dimethylcyclobutylethanal) from α-pinene, *cis*-3-caronaldehyde **C7** (*cis*-2,2-dimethyl-3-(2-oxopropyl)cyclopropanylethanal) from 3-carene, pina ketone **B9** (6,6-dimethylbicyclo[3.1.1]heptan-2-one), also known as nopinone, from β-pinene, sabina ketone **S9** (5-isopropylbicyclo[3.1.0]-hexan-2-one) from sabinene, and limona ketone **L9** (4-acetyl-1-methylcyclohexene), limononaldehyde **L7** (3-isopropenyl-6-oxo-heptanal), and ketolimononaldehyde **L7′** (3-acetyl-6-oxoheptanal) from limonene.

Hydroxyketoaldehydes have previously been tentatively identified as products from α-pinene/O_3 (*24, 45, 47*) and 3-carene/O_3 (*24, 45*). We have recently (*27*) confirmed the identification of 10-hydroxy-pinonaldehyde **A8** (*cis*-2,2-dimethyl-3-hydroxyacetylcyclobutylethanal) from the exactly matching retention times and mass spectrometric data with those of the major oxidation product from ozonolysis of myrtenol (10-hydroxy-α-pinene). Due to the extra hydroxy group in the molecular structure their equilibrium vapor pressures are considerably lower than those of the corresponding ketoaldehydes. As such, hydroxyketoaldehydes may accumulate in the particle phase. The tentatively identified hydroxyketoaldehydes were *cis*-10-hydroxypinonaldehyde **A8** (*cis*-2,2-dimethyl-3-hydroxyacetylcyclobutylethanal) from α-pinene, *cis*-10-hydroxy-3-caronaldehyde **C8** (*cis*-2,2-dimethyl-3-(hydroxy-2-oxopropyl)cyclopropanylethanal) from 3-carene, and 7-hydroxylimononaldehyde **L8** (7-hydroxy-3-isopropenyl-6-oxoheptanal) and 7-hydroxyketolimononaldehyde **L8′** (3-acetyl-7-hydroxy-6-oxoheptanal) from limonene (Figure 4). The position of the hydroxy-group in the proposed structures for the hydroxyketoaldehydes from 3-carene and limonene is based upon similarities with 10-hydroxypinonaldehyde **A8** in retention times and MS data. Other isomers may also be possible.

In the gas-phase low amounts of hydroxy-ketones were also detected such as 3-hydroxy-pina ketone **B10** (3-hydroxy-6,6-dimethylbicyclo[3.1.1]heptan-2-one), and 3-oxo-pina ketone (6,6-dimethylbicyclo[3.1.1]heptan-2,3-dione) from β-pinene and tentatively identified 3-hydroxy-sabina ketone **S10** (3-hydroxy-5-isopropylbicyclo[3.1.0]hexan-2-one) and 3-oxo-sabina ketone (5-isopropylbicyclo[3.1.0]hexan-2,3-dione). These oxidized forms of pina ketone and sabina ketone have previously been reported in the gas-phase (*45*−*47*). Only hydroxy-ketones (Figure 4) were found in measurable concentrations in SOA.

Binary Diacid Clusters. Hoffmann et al. (*23*) have recently hypothesized on formation of binary, tertiary, and higher clusters of nucleating multifunctional carboxylic acids in the reactions of terpenes with ozone. Experimental indication for binary clusters derived from online APCI-MS analysis of SOA from α-pinene/O_3 and was based upon a signal at m/z 357 corresponding to the pseudomolecular cluster ion $[M1 + M2 - H]^-$ of pinic acid **AB1** and norpinic acid **AB2** (Figure 4). Furthermore, offline HPLC-APCI-MS analysis of SOA sampled on filters gave a peak in the ion-chromatogram at m/z 357. MS^2 analysis of the ion m/z 357 revealed fragment ions corresponding to pinate (m/z 185) and norpinate (m/z 171).

In contrast to Hoffman et al. no evidence of such clusters has been found, neither in the present nor in other studies of SOA from terpene/O_3 reactions (*24*−*27, 45*). A number of unanswered questions in the study of Hoffmann et al. point to measurement artifacts as an alternative explanation of their observations. It is unclear why clusters of a minor oxidation product (norpinic acid **AB2**) are observed and not clusters between the main carboxylic acids (pinonic **A3**, pinic **AB1**, and hydroxypinonic acid **AB6**). Furthermore a binary diacid cluster only held together by hydrogen bonds, if existing, would dissociate in the offline analysis during 2−15 h adsorptive sampling on Tenax, extraction with methanol, and elution through a reversed phase LC column with a 30 mM ammonium acetate buffered solution. It is well-known that atmospheric pressure ionization techniques suffer from inherent artifact formation of adducts and clusters. The critical step in online APCI analysis of particles is the evaporation/desolvation of the analyte to generate significant gaseous concentrations available for ionization in the corona discharge region. The APCI is originally developed as an interface of liquid chromatography with mass spectrometry, and the evaporation/desolvation processes have been optimized for trace concentrations of analytes in volatile solvents such as methanol, water, etc. To reduce the artifact formation of clusters and adducts the chemist typically operate the HPLC-APCI-MS at low concentration levels and at optimized source conditions (temperature, sheath gas flow, choice of solvent). When using the APCI source for online analysis of particles consisting of bulk concentrations of nonvolatile analytes evaporation/desolvation processes are by no means facilitated and problems with adducts and cluster are augmented. A demonstration of the strong formation of clusters of multifunctional carboxylic acids in the APCI source is shown in Figure 7. The data were obtained by measuring the ion intensity over a source temperature range of 500−850 K, after direct injection of dilute methanolic solutions of mixtures of pinic acid **AB1** and pinonic acid **A3**. The heat of formation calculated from the Arrhenius plots points to intermediate strength hydrogen bonds as the governing forces of these binary clusters A clear demonstration of such an artifact is shown in Figure 5. Pinic acid **AB1** (m/z 185) and norpinic acid **AB2** (m/z 169) are well separated, and no signal for their binary cluster (m/z 357) in the chromatogram can be seen. However in the peak obtained by postcolumn flow injection of the SOA extract (no chromatographic separation) a clear artifact signal is formed.

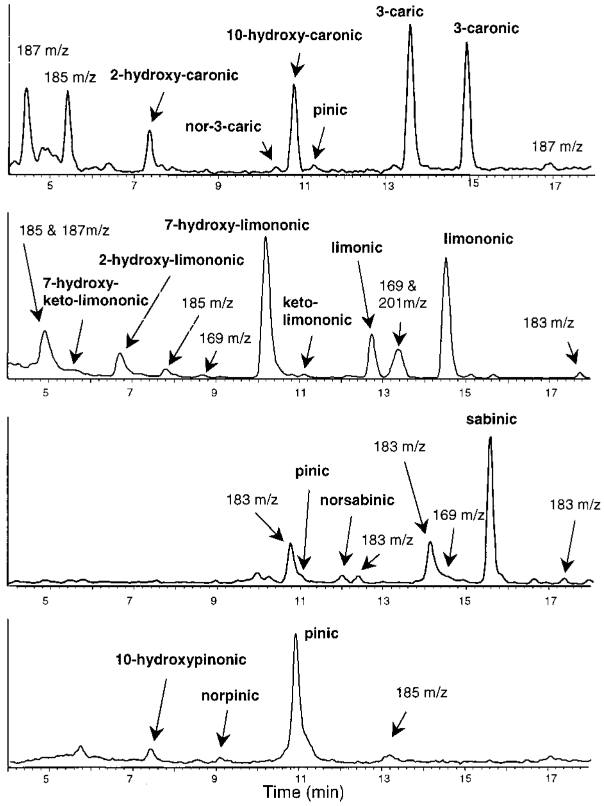

FIGURE 6. HPLC-ESI-MS chromatograms (TIC) of carboxylic acids in aerosol from ozonolysis of 3-carene (top), limonene (second), sabinene (third), and β-pinene (bottom).

Unidentified Compounds. In the chromatograms a number of minor peaks were present, to which no chemical

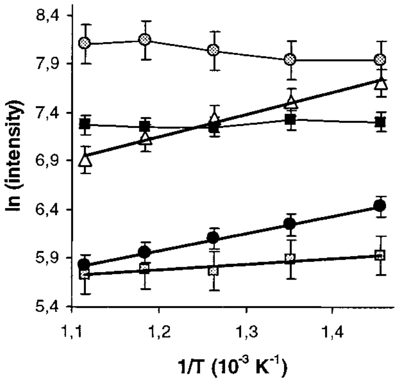

FIGURE 7. Arrhenius plots for the ion formation by APCI(−). Gray bullets: pinate $[M - H]^-$; black bullets: pinate−pinic acid cluster $[2M - H]^-$; gray squares: pinonate $[M - H]^-$; black bullets: pinonate−pinonic acid cluster $[2M - H]^-$; white triangles: pinate−pinonic acid cluster $[M1 + M2 - H]^-$.

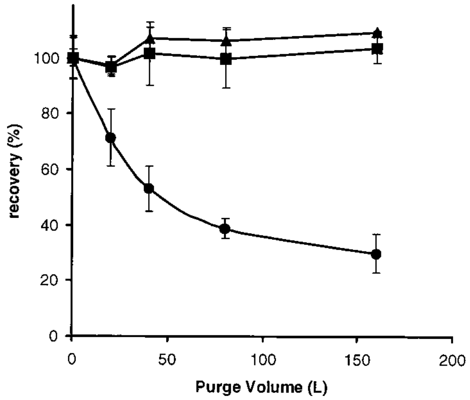

FIGURE 8. Desorptive loss of *cis*-pinic acid (squares), *trans*-pinic acid (triangles), and *cis*-pinonic acid (bullets) from spiked filters after purging with clean air.

structure could be assigned. They point to carboxylic acids with a molecular mass of *m*/*z* 172 (not C_8-dicarboxylic acids), *m*/*z* 184 (not corresponding to any identified ketocarboxylic acid), *m*/*z* 186 (not corresponding to any identified C_9-dicarboxylic acid), *m*/*z* 188, *m*/*z* 202, and *m*/*z* 216. It is not possible to quantify unknown compounds. Based on the intensities in the chromatograms the sum of these unidentified carboxylic acids may represent up to 20−30% of the mass of polar reaction products in SOA.

Product Yields. Sampling of aerosol is associated with a number of inherent errors. The relatively high surface-to-volume ratio of the PTFE bags used as reaction chambers may lead to loss of particles by coagulation and subsequent settling on the reactor walls. An upper limit of this loss has been estimated to be in the order of 30−40% (*39*), when sampling after 6 h. Also, organic vapors may be lost to the reactor walls. Only scarce data is available in the literature on this topic. Based on measurements of loss of pinonaldehyde **A7** to the walls of a glass reactor (*21*) we estimate that between 10 and 30% of the nonvolatile polar reaction products may be lost to the walls in the present study. Organic compounds may also evaporate (desorb) from already sampled particles. To get a worst case estimate of desorptive loss during sampling, PTFE filters were impregnated with 10 μg of pinic acid **AB1** and pinonic acid **A3** and purged at 298 K with large volumes of clean air. As seen in Figure 8, the dicarboxylic acid remained unaffected on the filters, whereas the ketocarboxylic acid was gradually lost. After 180 L purging approximately 60% of pinonic acid **A3** was lost. During sampling of SOA in the present smog chamber experiments desorptive loss is much lower, since the air passing the filters is already saturated with reaction products. Finally, organic vapors may condense/adsorb onto the filter surface containing the already collected particles. This may change the composition of SOA and lead to overestimations of yields. No data are available in the literature, which allows an estimation of the magnitude of this problem. To overcome this, denuders may be used to strip the gas phase out of the sampling flow (*17, 23, 25*). Possible drawbacks of this solution is an elevated evaporative loss of semivolatile oxidation products in SOA and artifact formations of terpene oxidation products by reaction of residual ozone with gas-phase compounds collected on the denuder walls similar to the artifacts demonstrated for adsorptive sampling of terpenes without ozone scrubbers (*32*−*34*). The relatively high proportion of pinic acid **AB1** reported in the gas-phase of recent smog chamber experiments by Jang and Kamens (*25*) may have been caused by denuder artifacts.

Quantitative determination of carboxylic acids in SOA is possible for compounds that have neat standards available. A comparison of the quantitative results by the LC-MS method and the GC-MS method for pinonic **A3** and pinic acid **AB1** (α-pinene and β-pinene experiments) showed agreements within 20−35%. In the absence of pure standards for other terpene oxidation products than pinic acid **AB1**, pinonic acid **A3**, and pinonaldehyde **A7**, a semiquantitative approach was taken. Dicarboxylic acids (C_9 and C_8) and ketocarboxylic acids (C_{10} and C_9) were quantified as their methyl-ester derivatives by GC-EI-MS (total ion current, TIC) using respectively *cis*-pinic acid **AB1** and *cis*-pinonic acid **A3** as surrogate standards. Hydroxyketocarboxylic acids show low recoveries in the methylation procedure due to losses during cleanup of the derivatized extracts and could therefore not be quantified by GC-MS. Instead HPLC-ESI-MS (TIC) was used with *cis*-pinonic acid **A3** as surrogate. Ketones, ketoaldehydes, and hydroxy-ketones were quantified by HPLC-APCI-MS (TIC). Pinonaldehyde **A7** and 2-hydroxy-3-pinanone were used as surrogate standard for ketoaldehydes and hydroxy-ketones, respectively. Pina ketone was quantified with authentic standards. The response for a chemical compound by atmospheric pressure ionization MS is more dependent on its chemical structure than by GC-EI-MS, thus the uncertainty in quantification of hydroxy compounds can be assumed to be higher than the uncertainty for the non-hydroxylated analogues. Table 1 presents the molar yields of the quantifiable oxidation products in SOA from the smog chamber experiments. The uncertainty associated with the estimated yields comprises uncertainties for a number of steps in the entire analytical procedure. The most significant error sources are estimated to be quantification of the monoterpene starting concentration (± 10%), sample volume determination (± 5%), interference of ozone during sampling (± 10−20%), particle collection and wall loss (<40%), extraction loss (<5−10%), derivatization loss (<10%), and surrogate calibration uncertainty (±20−50%).

It appears in Table 1, that the load of organic compounds to SOA formed by ozonolysis of terpenes amount to a few percent of the reacted mass. For each terpene there is a high variability in the total yield of reaction products, which cannot be accounted for by measurement error alone, but may be explained by different reaction conditions such as initial concentrations of terpene, ozone, and OH scavenger. There seems to be a trend in the data of the absolute yields to decrease with scavenging of OH radicals. This is consistent with current theories for terpene oxidation (*20*) and secondary OH formation, which may be responsible for a part of the observed products in particular the decarboxylated species such as C_8-dicarboxylic acids and C_9-ketocarboxylic acids and C_9-hydroxyketocarboxylic acids. There is also a tendency for the absolute yields to decrease with a decreasing initial terpene concentration, which is consistent with recent observations on SOA formation governed by adsorptive partition processes (*4, 5, 9*).

A remarkable product analogy was observed in SOA from the five investigated terpenes. For the terpenes with an endocyclic C=C double bond (α-pinene and 3-carene) the molar fraction distribution was 0.2−0.4 of C_9-dicarboxylic acids, 0.3−0.5 of C_{10}-ketoaldehydes, 0.2−0.3 of C_{10}-hydroxyketocarboxylic acids, 0.1−0.2 of C_{10}-ketocarboxylic acids, and 0.04−0.06 of C_{10}-hydroxyketoaldehydes. For the terpenes with an exocyclic C=C double bond (*β*-pinene, and sabinene) the molar fraction distribution was 0.5−0.7 of C_9-dicarboxylic acids, 0.05−0.2 of C_9-ketones, 0.05−0.15 of C_9-hydroxyketones, 0.05−0.1 of C_{10}-hydroxyketocarboxylic acids, and 0.02−0.06 of C_8-dicarboxylic acids. Limonene, containing both an endocyclic and an exocyclic C=C double bond, showed a product distribution between the two groups, with an additional group of compounds (molar fraction from 0.01 to 0.02) deriving from oxidation of both double bonds.

To date, only a few studies have been published on the composition of SOA after terpene/ozone reactions, which includes detailed quantitative data on carboxylic acids (*25, 45*). The experimental conditions used in the investigations are too different to allow for a meaningful comparison of results. However, they all point to the conclusion, that a number of multifunctional carboxylic acids are accumulating in SOA at low percentage yields (1−5%), which together with other polar reaction products such as multifunctional carbonyls may account for a substantial fraction of the SOA mass. More quantitative data is needed to investigate the role of these compounds in aerosol formation processes.

Mechanistic Considerations. Based on the detailed data on main reaction products and key intermediates, which has become available over the latest few years (*11, 23−27, 45*), it has become possible to suggest chemical reaction mechanistic pathways for aerosol formation. Generally approved gas-phase mechanisms over Criegee biradical intermediates lead directly to C_{10}-ketoaldehydes and C_{10}-ketocarboxylic acids such as e.g. pinonaldehyde **A7** and pinonic acid **A3** from α-pinene. Pathways leading to C_9-dicarboxylic acids such as pinic acid **AB1** are less evident and necessitate a number of rearrangement reactions of the Criegee biradicals and subsequent oxidation either in the gas phase (*24, 25, 45*) or the aerosol phase (*25*). The hydroperoxide channel of the excited C_9-Criegee intermediate as proposed by Winterhalter et al. (*48*) is the only pure gas-phase pathway proposed to data that can lead to formation of C_9-dicarboxylic acids. However the experimental observation of key intermediates is still lacking. The present observations of significant yields of C_{10}-hydroxyketoaldehydes and C_{10}-hydroxyketocarboxylic acids may be taken as an evidence of Criegee biradical rearrangements. Although it is out of the scope of the present investigation to discuss formation mechanisms, an interesting observation of mechanistic relevance was done during some of the experiments. When $H_2{}^{18}O$ was added to the smog chambers at a 5% relative humidity after drying out all nonlabeled water ($H_2{}^{16}O$) precisely one ^{18}O atom was incorporated into the molecular structure of dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids at fractions between 10 and 20%, but not in significant amounts (2−3%), into the molecular structure of ketoaldehydes or hydroxyketoaldehydes (Table 2). When secondary OH radicals were not scavenged the fraction of ^{18}O-analogues increased, possibly due to a OH-^{18}OH shift reaction ($H_2{}^{18}O + OH \leftrightarrow H_2O + {}^{18}OH$). The incorporation of ^{18}O was observed in the MS^2 daughter scans of the *quasi*-molecular ion by fragments from neutral loss of H_2O, $H_2{}^{18}O$, CO_2, and $O{=}C{=}{}^{18}O$. An example is given in Figure 9 for $[M - H]^- = 187$ of ^{18}O-pinic acid from the α-pinene/O_3/$H_2{}^{18}O$ reaction. Further experiments with $H_2{}^{18}O$ are in progress in our laboratory. These preliminary results indicate that mechanistic pathways for carboxylic acid formation through ozone/terpene reactions may include a reaction step with H_2O addition and that water vapor may play an important role in SOA formation, not only physically but also chemically. This factor has been neglected in the experimental setup of SOA experiments performed till date and should be investigated further.

TABLE 2. Incorporation[a] of ^{18}O into Major Oxidation Products in Aerosol from α-Pinene/O_3/$H_2{}^{18}O$

	secondary OH radicals scavenged with methyl-*c*-hexane	no OH scavenger
pinic acid	21%	34%
pinonic acid	9%	18%
10-hydroxypinonic acid	19%	28%
pinonaldehyde	2%	3%

[a] Expressed as the fraction of the oxidation product containing one ^{18}O molecule relative to its total yield, $Y_{M+2}/(Y_M+Y_{M+2})$.

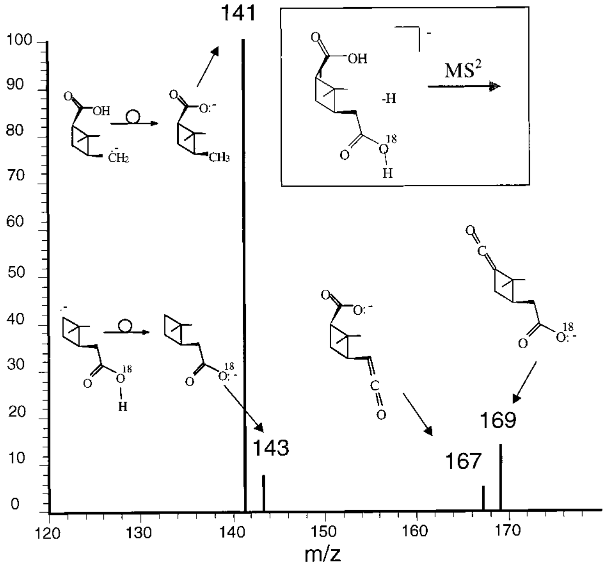

FIGURE 9. MS^2 daughter scan of the *quasi*-molecular ion $[M - H]^- = 187$ of ^{18}O-pinic acid from the α-pinene/O_3/$H_2{}^{18}O$ reaction. Note the fragments from neutral loss of H_2O, $H_2{}^{18}O$, CO_2, and $O{=}C{=}{}^{18}O$.

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Supporting Information Available

Mass spectral data for tentative identification of polar oxidation products in secondary aerosol from the gas-phase reaction of terpene and ozone. This material is available free of charge via the Internet at http://pubs.acs.org.

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