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Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products

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Abstract. Atmospheric oxidation of monoterpenes contributes to formation of tropospheric ozone and secondary organic aerosol, but their products are poorly characterized. In this work, we report a series of outdoor smog chamber experiments to investigate both gaseous and particulate products in the ozone oxidation of four monoterpenes: α-pinene, β-pinene, Δ^3-carene, and sabinene. More than ten oxygenated products are detected and identified in each monoterpene/O_3 reaction by coupling derivatization techniques and GC/MS detection. A denuder/filter pack sampling system is used to separate and simultaneously collect gas and aerosol samples. The identified products, consisting of compounds containing carbonyl, hydroxyl, and carboxyl functional groups, are estimated to account for about 34–50%, 57%, 29–67%, and 24% of the reacted carbon mass for β-pinene, sabinene, α-pinene, and Δ^3-carene, respectively. The identified individual products account for $>$83%, $\sim$100%, $>$90%, and 61% of the aerosol mass produced in the ozone reaction of β-pinene, sabinene, α-pinene, and Δ^3-carene. The uncertainty in the yield data is estimated to be $\sim \pm 50\%$. Many of the products partition between gas and aerosol phases, and their gas-aerosol partitioning coefficients are determined and reported here. Reaction schemes are suggested to account for the products observed.

Key words: monoterpenes, aerosols, organic aerosols.

1. Introduction

Emissions of biogenic organic compounds have been estimated to dominate over those from anthropogenic sources on a global basis (Guenther *et al.*, 1995). As important constituents of biogenic VOC emissions, the $C_{10}H_{16}$ monoterpenes contribute to formation of tropospheric ozone and secondary organic aerosol (SOA) (Kamens *et al.*, 1981; Chameides *et al.*, 1988; Pandis *et al.*, 1991; Zhang *et al.*, 1992; Hoffmann *et al.*, 1997; Griffin *et al.*, 1999). Whereas the rate constants of monoterpenes with OH radicals, NO_3 radicals, and O_3 are reasonably well established, the reaction products are less well understood (Atkinson, 1997; Calogirou *et al.*, 1999). Information on both gaseous and particulate products is important to

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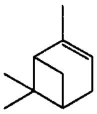
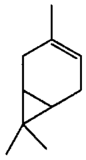
elucidate the mechanism of oxidation and to understand the formation of secondary organic aerosol.

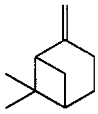
In a previous paper, we reported the identification of ozone oxidation products of α-pinene and Δ^3-carene (see below for chemical structures) (Yu *et al.*, 1998). In this work we have investigated ozone oxidation products of two additional bicyclic monoterpenes, β-pinene and sabinene, for which little product information is known.



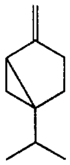
α-pinene



Δ^3-carene



β-pinene



sabinene

At an initial β-pinene mixing ratio of several ppmv, nopinone is the only product that has previously been clearly identified from O_3 oxidation of β-pinene, besides low-molecular products such as formaldehyde, CO, and CO_2 (Hatakeama *et al.*, 1989; Grosjean *et al.*, 1993; Hakola *et al.*, 1994). For the sabinene/O_3 reaction, sabina ketone is the only known product (Hakola *et al.*, 1994).

Few studies have been carried out to determine yields of gaseous and particulate products from ozone oxidation of the monoterpenes, and to our knowledge, no study has been reported to examine gaseous and particulate oxidation products simultaneously. The semi-volatile nature of many of the oxidation products dictates that they partition between the gas and aerosol phases. The filter-only technique, which is the most common aerosol sampling method, results in positive artifacts from adsorption of gaseous semi-volatile compounds on the filter (McDow and Huntzicker, 1990; Hart and Pankow, 1994). We have employed a denuder/filter pack system to separate gaseous and particulate semivolatile compounds and to minimize sampling artifacts. Using this sampling device, we have measured the product yields from the ozone oxidation of the four monoterpenes in both gas and aerosol phases, and determined their gas-aerosol partitioning coefficients.

Detection and identification of products from oxidation of biogenic hydrocarbons are hindered by the fact that many contain functional groups such as carbonyl and carboxylic acids that are poorly resolved by standard gas chromatography. We have recently reported a method to detect and identify organics containing –C=O (aldehyde and ketone), –OH (hydroxy) and –COOH (carboxyl) groups (Yu *et al.*, 1998). In this method, –C=O groups are derivatized using O-(2,3,4,5,6-pentafluorobenzyl) hydroxy amine (PFBHA), and –COOH and –OH groups are derivatized using a silylation reagent, N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), to give trimethylsilyl (TMS) derivatives. The resulting derivatives are easily resolved by a GC column, and identified by their chemical ionization (CI) and electronic ionization (EI) mass spectra. The CI mass spectra of these derivatives exhibit several pseudo-molecular ions, allowing unambiguous determination of molecular weights. The EI mass spectra allow functional group identification by exhibiting ions characteristic of each functional group: *m/z* 181 for carbonyl, and *m/z* 73 and 75 for carboxyl and hydroxy groups. In addition, each functional group is associated with a unique set of pseudo-molecular ions in CI spectra. The PFBHA-carbonyl derivatives give rise to pseudo-molecular ions at *m/z* M+181, M-181 and M-197, whereas the TMS derivatives of OH/COOH containing compounds have pseudo-molecular ions at *m/z* M+73, M-15 and M-89. We refer the reader to Yu *et al.* (1998) for a detailed description of the mass spectra fragment patterns.

2. Experimental Section

2.1. SMOG CHAMBER EXPERIMENTS AND SAMPLE COLLECTION

Samples were collected from a series of β-pinene/O_3, sabinene/O_3, α-pinene/O_3, and Δ^3-carene/O_3 experiments, conducted in the dark in a 60-m^3 Teflon reactor, which has been described previously (Hoffmann *et al.*, 1997; Griffin *et al.*, 1999). When fully inflated, the reactor has a surface to volume ratio (S/V) of 1.8 m^{-1}. This reactor was normally divided in the center so that two experiments could be run under identical environmental conditions. The temperature in the reactor was maintained between 305 and 310 K to approximate that of a typical afternoon smog chamber experiment. To achieve this, the entire reactor was covered with an insulating cover as well as a black tarpaulin. In addition, four Holmes (Milford, MA) Model HFH-501FP space heaters were placed in the open area underneath the reactor. In a typical experiment, seed particles of $(NH_4)_2SO_4$ were injected into the chamber to obtain initial particle concentrations of approximately 9,000–17,000 particle cm^{-3}. The initial size distribution of the seed aerosol was centered around 100 nm. The aerosol size distribution and total number concentrations of each side of the reactor were monitored at a one-minute frequency using a TSI (St. Paul, MN) Model 3071 cylindrical scanning electrical mobility spectrometer (SEMS) and a TSI Model 3760 condensation nucleus counter (CNC). Particle losses in the SEMS, SEMS response functions, particle charging efficiencies, CNC charging efficiencies, and particle deposition in the reactor have been taken into account in the analysis of the aerosol data (Wang *et al.*, 1992). The initial monoterpene mixing ratio ranged from 50 to 110 ppbv, and an appropriate amount of 2-butanol was also added to the reactor to scavenge $>$95% of OH radicals produced from the monoterpene-O_3 reaction (Chew and Atkinson, 1996; Atkinson, 1997). Finally, ozone was injected to the reactor using an Enmet Corporation (Ann Arbor, MI, U.S.A.) Model 04052-011 O_3 generator until the O_3 mixing ratio reaches at approximately four times that of the initial hydrocarbon for all experiments except one α-pinene/O_3 and one β-pinene/O_3 experiment, in which excessive hydrocarbon was established in the reactor. Table I summarizes the initial conditions of each experiment.

Table I. Initial conditions and results of ozone-terpene reactions

HC	Date	T (K)	O_3 initial ppbv	HC initial ppbv	HC final ppbv	ΔHC ppbv	Sample start time (min)	ΔM_o μg m^{-3}	Aerosol yield
α-Pinene	6/9/98a	308	237	59.2	2.2	57.0	291	54.2	0.176
	6/9/98b	308	269	67.2	2.1	65.1	339	65.1	0.186
	6/17/98a	306	74	107.1	62.0	45.1	53	38.8	0.159
β-Pinene	6/11/98b	307	352	87.9	10.0	77.9	388	18.9	0.045
	6/17/98b	306	56	104.6	79.8	24.8	303	11.2	0.083
Δ^3-Carene	6/15/98b	306	360	89.9	0.4	89.5	299	63.3	0.130
Sabinene	6/15/98a	306	370	92.4	0.0	92.4	232	17.6	0.035

Reactor air was withdrawn through a sampling system consisting of a glass annular denuder (University Research Glassware, Chapel Hill, NC, U.S.A.) followed by a 47 mm Pallflex Teflon impregnated glass fiber filter at a flow rate of 25 L min^{-1} for 1 h. The denuder is 40 cm long and consists of 5 annular channels with 2 mm space between channels. The sand-blasted denuder walls were coated with sub-micron XAD-4 particles beforehand using the procedure described by Gundel *et al.* (1995).

2.2. SAMPLE TREATMENT AND ANALYSIS

Denuder and filter samples were spiked with 10 μL of 40 ng/μL tricosane in dichloromethane (DCM) immediately after sample collection. Filters were soxhlet-extracted with 160 mL 1 : 1 acetonitrile and DCM solvents for 12–16 hrs. Before extraction, 150 μL of 19 mM PFBHA acetonitrile/aqueous solution (a minimum amount of water was used to dissolve PFBHA · HCl) was added to the soxhlet extractor along with the extraction solvents. Denuders were extracted with 4 × 40 mL of a solvent mix made of DCM, acetonitrile, and hexane (50% : 38% : 12%) by manually inverting the denuder 40 times. After addition of 150 μL of 19 mM PFBHA solution, the denuder extracts were left at room temperature overnight. Then both the filter and denuder extracts were reduced to ca. 5 mL by rotary evaporation. The extracts were blown to nearly dryness under a gentle N_2 stream, followed by reconstitution with 280 μL 1 : 1 hexane and DCM solvent mixture, and addition of 20 μL of BSTFA and 10 μL of 3 ng/μL 1-phenyldodecane (injection internal standard). The mixtures were then heated at 70 °C for 2.5 hrs. After cooling briefly, 20 μL of the mixture was injected for GC/MS analysis.

A Varian Saturn 2000 gas chromatograph/ion trap mass spectrometer was used for both EI and methane CI analysis. The GC temperature was programmed at 60 °C for 1 min, to 250 °C at 10 °C/min, to 300 °C at 5 °C/min, and held at 300 °C for 10 min. Samples were injected in the splitless injection mode. The injector was switched to split mode 1 min after an injection was made. The injector port temperature was programmed at 60 °C for 1 min, ramped to 320 °C at 180 °C/min, and held at 320 °C until the end of the analysis. The mass range was 50–650 amu. A 30 m × 0.25 mm × 0.25 μm DB-5 fused silica column was used for all samples.

2.3. DENUDER AND FILTER COLLECTION EFFICIENCIES

The collection efficiency of the 40-cm long denuder was determined by connecting this denuder and a 20-cm long denuder in series (the limited space between the sampling port and the ground can only accommodate a 20-cm long denuder). The collection efficiency was calculated as $A_L/(A_L + A_S)$, where A_L and A_S represent the amounts collected by the long and the short denuders, respectively. Semi-volatile products can volatilize from a filter due to changes in gas/particle equilibrium conditions as a result of the denuder stripping off gas-phase semi-

Table II. Denuder and filter collection efficiencies of selected products

Compound	Collection efficiency (%)	
	Denuder	Filter
Pinic acid	98.7 ± 0.2	85
2,2-Dimethyl-3-formyl-cyclobutyl methanoic acid	97.1 ± 1.9	NA[a]
Norpinonic acid	94.0 ± 4.0	NA
Pinonic acid	97.8 ± 1.3	59
Norpinonaldehyde	95.8 ± 1.0	89
Pinonaldehyde	97.7 ± 0.5	95

[a] Not available.

Table III. Relative recoveries of select multifunctional compounds vs recovery standard

Compound	Denuder samples $N = 6$[a]	Filter samples $N = 5$[a]
Pinic acid	0.66 ± 0.04	0.80 ± 0.07
Pinonic acid	0.67 ± 0.19	0.74 ± 0.14
2-Hydroxy-cyclohexanone	0.64 ± 0.10	0.74 ± 0.07
5-Methyl-1,3-cyclohexanedione	0.41 ± 0.06	0.61 ± 0.08
5-Isopropyl-1,3-cyclohexanedione	0.44 ± 0.04	0.63 ± 0.10
7-Oxo-octanoic acid	0.66 ± 0.12	0.83 ± 0.07
Heptanedioic acid	0.69 ± 0.05	0.77 ± 0.17
Octanedioic acid	0.59 ± 0.05	0.82 ± 0.14

[a] Number of experiments conducted.

volatiles. The filter ‘blow-off’ was collected by a pre-baked glass fiber filter placed downstream from the Teflon filter. The filter collection efficiency was then calculated as $F_t/(F_t + F_g)$, where F_t and F_g represent the amounts collected by the front Teflon filter and the rear glass fiber filter, respectively. The collection efficiencies were computed using the photooxidation products of α-pinene/NO$_x$ in the outdoor reactor under sunlight irradiation. The reaction mixture contained pinic acid, pinonic acid, norpinonic acid, 2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid, pinonaldehyde, and norpinonaldehyde. Table II lists the denuder and filter collection efficiencies for each individual product. The results indicate that a 20-cm long denuder is sufficient to collect any breakthrough from the first denuder.

2.4. RECOVERIES OF DENUDER AND FILTER SAMPLES

Recoveries of select compounds were determined by spiking on filters and denuders known amounts of liquid standards and the recovery standard tricosane. The same extraction and concentration procedures as those described in Section 2.2 were then applied. Relative recoveries for select multifunctional compounds versus the recovery standard tricosane are given in Table III. 2-Hydroxy-cyclohexanone is included to serve as a surrogate for hydroxy pina ketones and hydroxy sabina ketones, and the two dicarbonyls, 5-methyl-1,3-cyclohexanedione and 5-isopropyl-1,3-cyclohexanedione, act as surrogates for dicarbonyl compounds, such as pinonaldehyde and norpinonaldehyde. Two dicarboxylic acids, heptanedioic acid and octanedioic acid, and one keto acid, 7-oxo-octanoic acid, are included to test whether compounds with the same type of functional groups exhibit similar recoveries. Comparison of the recoveries of heptanedioic and octanedioic acid with that of pinic acid, a C_9 cyclic dicarboxylic acid, shows that the three dicarboxylic acids exhibit similar recoveries for both denuder and filter samples. The two keto acids, 7-oxo-octanoic acid and pinonic acid, also have similar recoveries. This adds confidence to the assumption that the recoveries for those compounds without available standards can be approximated with those of known standards that have similar functional groups.

For each compound tested, the denuder samples show lower recovery than filter samples. This indicates the mouth washing extraction technique performed on denuders is not as efficient in extracting the polar compounds as the soxhlet extraction method performed on filter samples. The large standard deviations associated with the recoveries are likely a result of a number of factors including extraction efficiency, volatilization during rotary evaporation, and losses from transfer and surface adsorption. Absolute recovery of a given compound is obtained by multiplying its relative recovery by that of tricosane in individual samples. All the denuder and filter samples have been corrected with the recoveries determined here.

3. Product Identification

The newly developed analytical derivatization method (Yu *et al.*, 1998) allows for detection and identification of three types of products: (1) those containing only carbonyl group(s) (e.g., simple aldehydes, ketones and dicarbonyls), (2) those containing only OH/COOH groups (e.g., dicarboxylic acids), and (3) those containing both carbonyl and OH/COOH groups (e.g., oxoacids and hydroxy carbonyls). Here OH/COOH denotes the presence of hydroxy or carboxy functional groups since the mass spectra for the TMS derivatives often can not differentiate between these two functional groups. Two types of ion chromatograms are constructed: *m/z* 181 ion chromatogram and *m/z* 73 and 75 ion chromatogram. Type (1) compounds show peaks only in the 181 ion chromatogram, type (2) compounds exhibit peaks only in the 73 and 75 ion chromatogram, and type (3) compounds show peaks in both chromatograms. The classification for each product is further substantiated by the unique pseudo-molecular ions in the CI mass spectra.

3.1. PRODUCTS FROM OZONE OXIDATION OF β-PINENE

Figure 1a is the reconstructed *m/z* 181 ion chromatogram, showing carbonyl-containing products from the β-pinene/O_3 reaction. Figure 1(b) is the reconstructed *m/z* 73 and 75 ion chromatogram, displaying all products bearing OH/COOH groups. Table IV lists molecular weight (MW), chemical structure, and the pseudo-molecular ion fragments in the CI mass spectra that are used to obtain molecular weight for the products. Product names are derived using the newly proposed nomenclature for terpene oxidation products by Larsen *et al.* (1998).

Among the products, compounds P_1 and P_2 are type (2) products, i.e., only contain OH/COOH groups. Compound P_1 is tentatively identified as norpinic acid (2,2-dimethyl-cyclobutane-1,3-dicarboxylic acid). The CI spectrum shows ions at *m/z* 389, 317, 301, 227, and 199, corresponding to M+73, M+1, M-15, M-89, and M-117 (Figure 2-P_1). The *m/z* M+73 ion is an adduct ion resulting from the addition of the $[Si(CH_3)_3]^{+\cdot}$ fragment ion to a neutral molecule. The *m/z* M+1 ion is the protonated molecular ion. The ions at *m/z* M-15, M-89, and M-117 are fragment ions resulting from loss of CH_3, $OSi(CH_3)_3$ and $C(O)OSi(CH_3)_3$ from the neutral molecules. Compound P_2 is identified as pinic acid, which has been confirmed by comparison with an authentic standard obtained from Aldrich (Figure 2-P_2).

Compounds P_3, P_{10}, and P_{11} have carbonyl groups, but no OH/COOH groups (type 1 compounds), as indicated by their presence in Figure 1(a) and absence in Figure 1(b). Compound P_3 is positively identified as nopinone (pina ketone) by comparison with an authentic standard. There are two GC peaks corresponding to nopinone, as PFBHA forms two geometric isomers with a given nonsymmetrical carbonyl (Le Lacheur *et al.*, 1993; Yu *et al.*, 1995). The relative intensity of the pseudo-molecular ions from two isomers of a PFBHA derivative may vary, but the mass fragment patterns are similar. Therefore, only one spectrum is given to illustrate the identification of a given carbonyl-PFBHA derivative. Figure 2-P_3 shows the CI spectrum of the second nopinone peak, with pseudo-molecular ions at *m/z* 514, 362, 334, 152 and 136, corresponding to M+181, M+29, M+1, M-181, and M-197. The *m/z* M+181 ion is an adduct ion formed between a neutral molecule and the fragment ion $[C_6F_5CH_2]^{+\cdot}$. The *m/z* M+29 ion is an adduct ion resulting from the addition of the methane reagent ion $[C_2H_5]^{+\cdot}$ to a neutral molecule. The ions at *m/z* M-181 and M-197 are fragment ions arising from loss of $C_6F_5CH_2$ and $C_6F_5CH_2O$ fragments from the neutral molecules. Compound P_{10} is tentatively identified as 2,2-dimethyl-cyclobutane-1,3-dicarboxaldehyde, with a MW of 530 for its PFBHA derivative (Figure 2-P_{10}). Compound P_{11} is tentatively identified as 3-oxo-pina-ketone, a diketone (Figure 2-P_{11}). Its PFBHA derivative has a MW of 542 when both carbonyl groups are derivatized. In addition, two peaks in Fig-

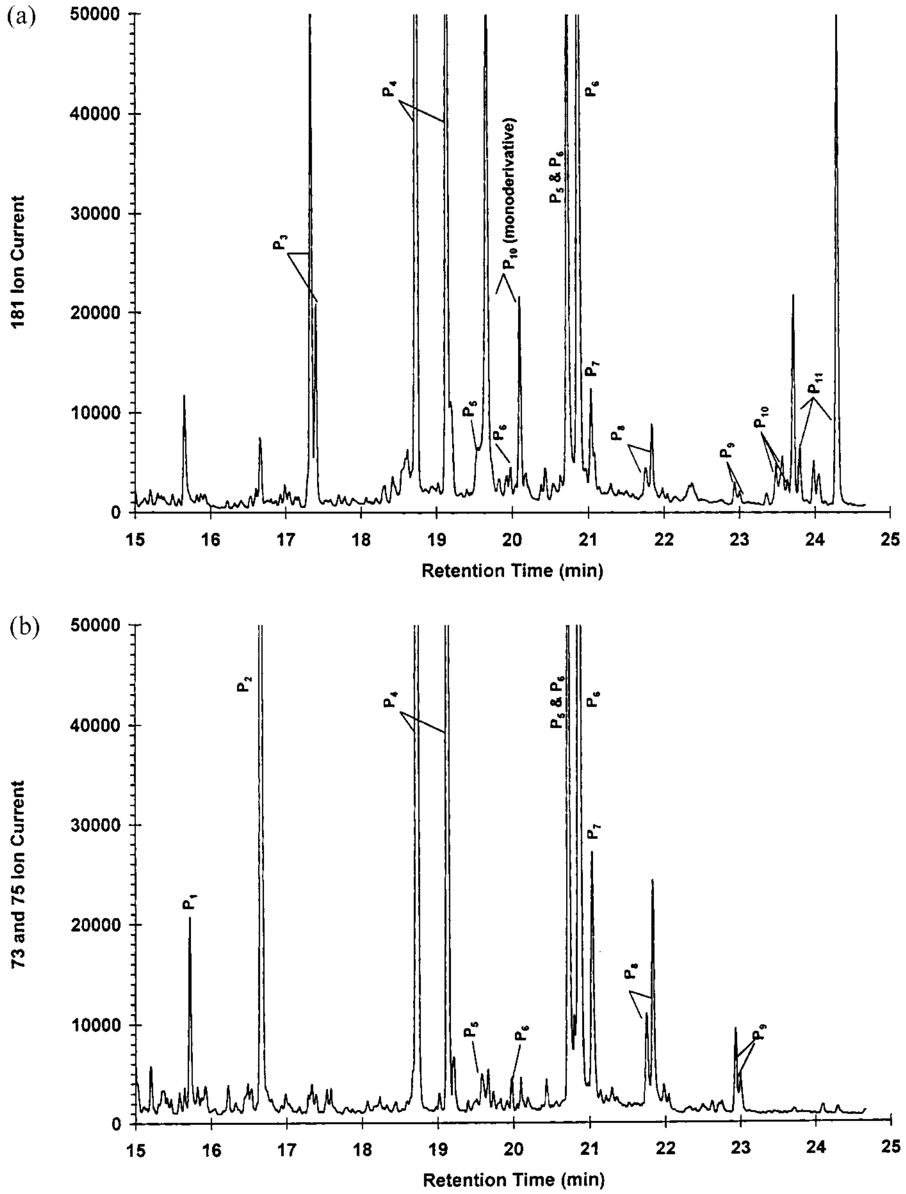


Figure 1. Chromatogram of products from β-pinene/O_3 reaction. See Table IV for peak identification. Top: Products containing carbonyl groups. Bottom: Products containing OH/COOH groups.

Table IV. Products from ozone oxidatio of β-pinene

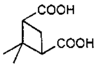
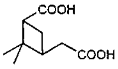
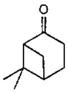
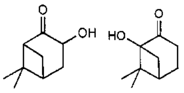
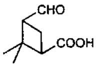
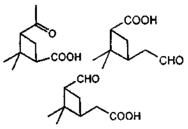
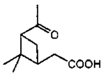
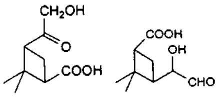
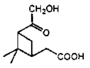
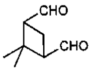
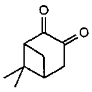
Name	Structure	Pseudo-molecular ions in CI mass spectrum	
P_1: $C_8H_{12}O_4$ norpinic acid MW = 172 deri. MW = 316[a]		M+73: 389 M-15: 301 M-117: 199	M+1: 317 M-89: 227
P_2: $C_9H_{14}O_4$[b] pinic acid MW = 186 deri. MW = 330		M+73: 403 M-15: 315	M+1: 331 M-89: 241
P_3: $C_9H_{14}O$[b] nopinone MW = 138 deri. MW = 333		M+181: 514 M+1: 334 M-197: 136	M+29: 362 M-181: 152
P_4: $C_9H_{14}O_2$ hydroxy pina ketone MW = 154 deri. MW = 421		M+181: 602 M-15: 406 M-197: 224	M+1: 422 M-89: 332
P_5: $C_8H_{12}O_3$ 2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid MW = 156 deri. MW = 423		M+73: 496 M-15: 408 M-117: 306 M-197: 226	M+1: 424 M-89: 334 M-181: 242
P_6: $C_9H_{14}O_3$ norpinonic acid and its isomers MW = 170 deri. MW = 437		M+73: 510 M-15: 422 M-117: 320 M-197: 240	M+1: 438 M-89: 348 M-181: 256
P_7: $C_{10}H_{16}O_3$[b] pinonic acid MW = 184 deri. MW = 451		M+73: 524 M-89: 362 M-197: 254	M+1: 452 M-181: 270 M-238: 213
P_8: $C_9H_{14}O_4$ hydroxy norpinonic acids MW = 186 deri. MW = 525	e.g. 	M+73: 598 M-15: 510 M-181: 344	M+1: 526 M-89: 436 M-197: 328

Table IV. (Continued)

Name	Structure	Pseudo-molecular ions in CI mass spectrum	
P_9: $C_{10}H_{16}O_4$ hydroxy pinonic acid MW = 200 deri. MW = 539		M+73: 612 M-15: 524 M-181: 358 M-326: 213	M+1: 540 M-89: 450 M-197: 342
P_{10}: $C_8H_{12}O_2$ 2,2-dimethyl-cyclobutane-1,3-dicarboxaldehyde MW = 140 deri. MW = 530		M+1: 530 M-197: 333	M-181: 349 M-224: 306
P_{11}: $C_9H_{12}O_2$ 3-oxo-pina ketone MW = 152 deri. MW = 542 mono-deri. MW = 347		M+29: 571 M-197: 345	M+1: 543

[a] deri. denotes derivative.

[b] Identification confirmed with an authentic standard.

ure 1(a) are ascribed to the mono-derivative of 3-keto-nopinone, with a MW of 347. For a dicarbonyl, PFBHA may derivatize only one of the two carbonyl groups and leave the other intact if unfavorable derivatization conditions occur. Among unfavorable conditions are steric hindrance and insufficient amount of derivatization agent and reaction time.

Compounds P_4, P_5, P_6, P_7, P_8, and P_9 have both carbonyl and OH/COOH groups (type 3 compounds), indicated by their presence in both Figures 1(a, b). Compound P_4 is tentatively identified as a hydroxy substituted nopinone, 3-hydroxy-pina ketone or 1-hydroxy-pina ketone. The derivatized form of P_4 has a MW of 421 (see Figure 2-P_4 for its CI mass spectrum). Compound P_5 is tentatively identified as 2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid, having a MW of 423 for its derivatized form (Figure 2-P_5). Three peaks, labeled P_6 in Figure 1, are identified to have a MW of 437, indicated by the presence of several pseudo-molecular ions in their CI spectrum at *m/z* 510, 438, 348, 256, and 240, corresponding to M+73, M+1, M-89, M-181, and M-197 (Figure 2-P_6). The observation of three peaks indicates that at least two isomers with the same number and type of functional groups are present. The following three isomers are possible candidates with structures consistent with the EI and CI mass spectra fragment patterns:

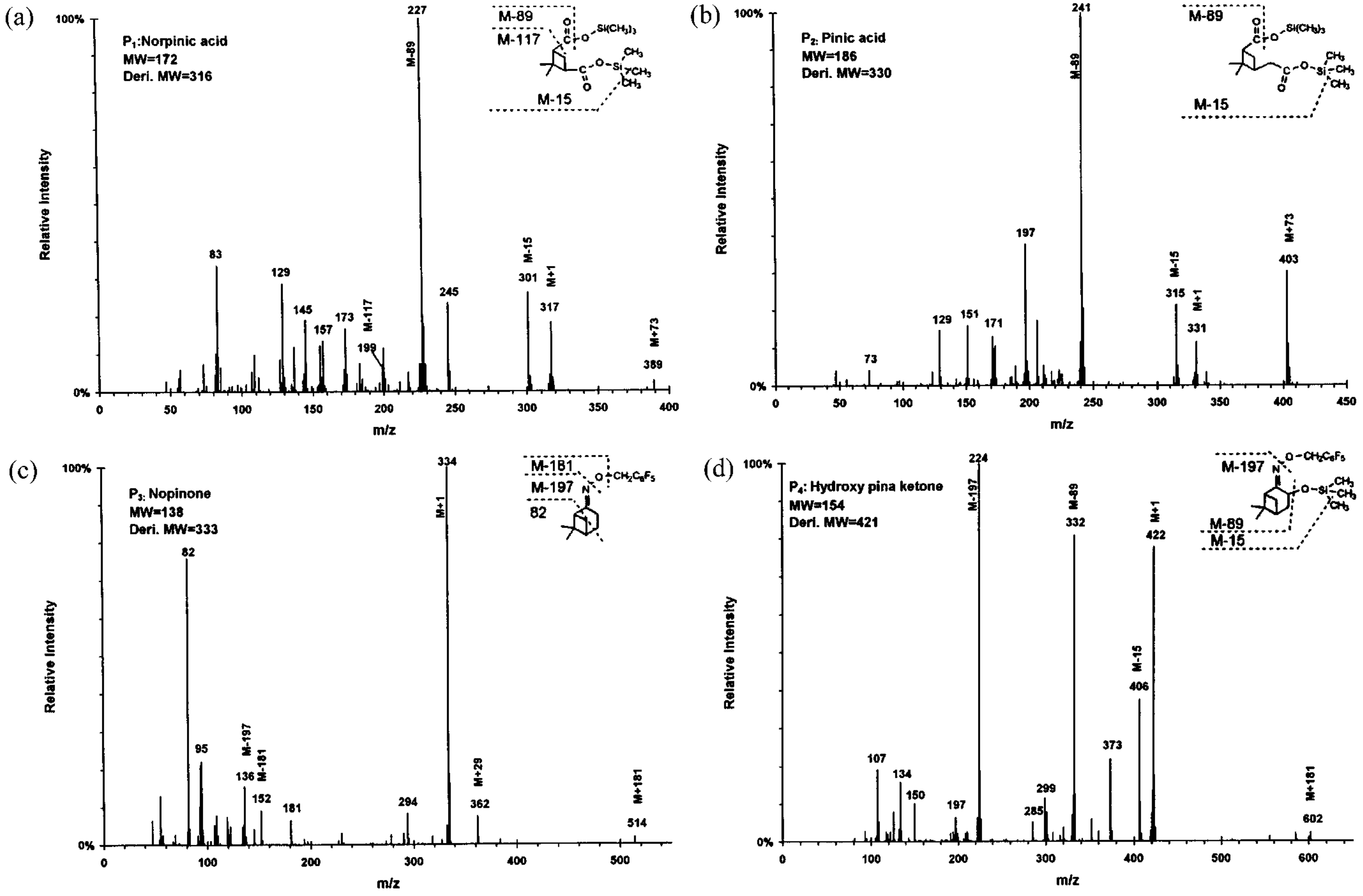


Figure 2. Methane CI mass spectra for the derivatives of products from ozone oxidation of β-pinene.

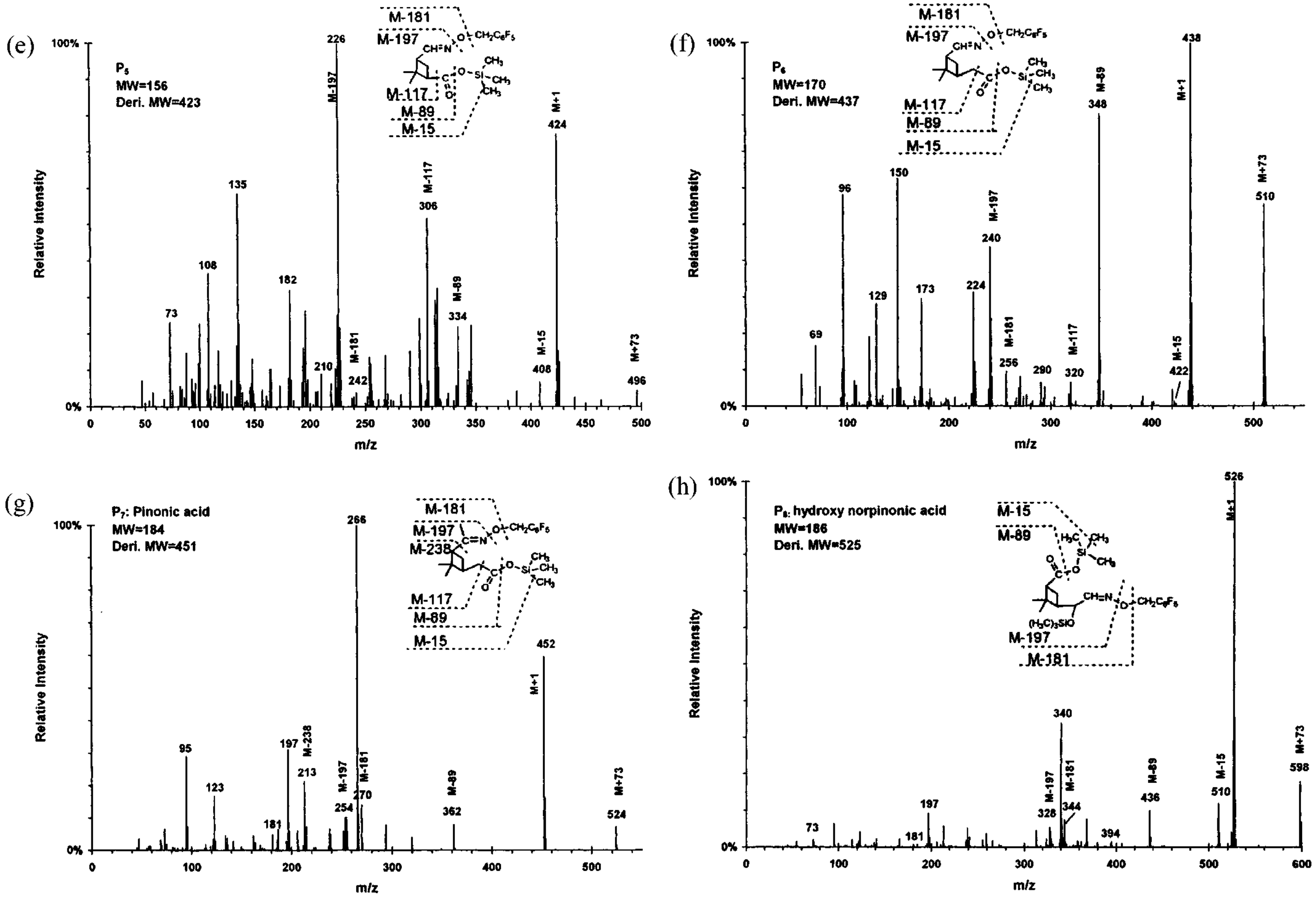


Figure 2. (Continued).

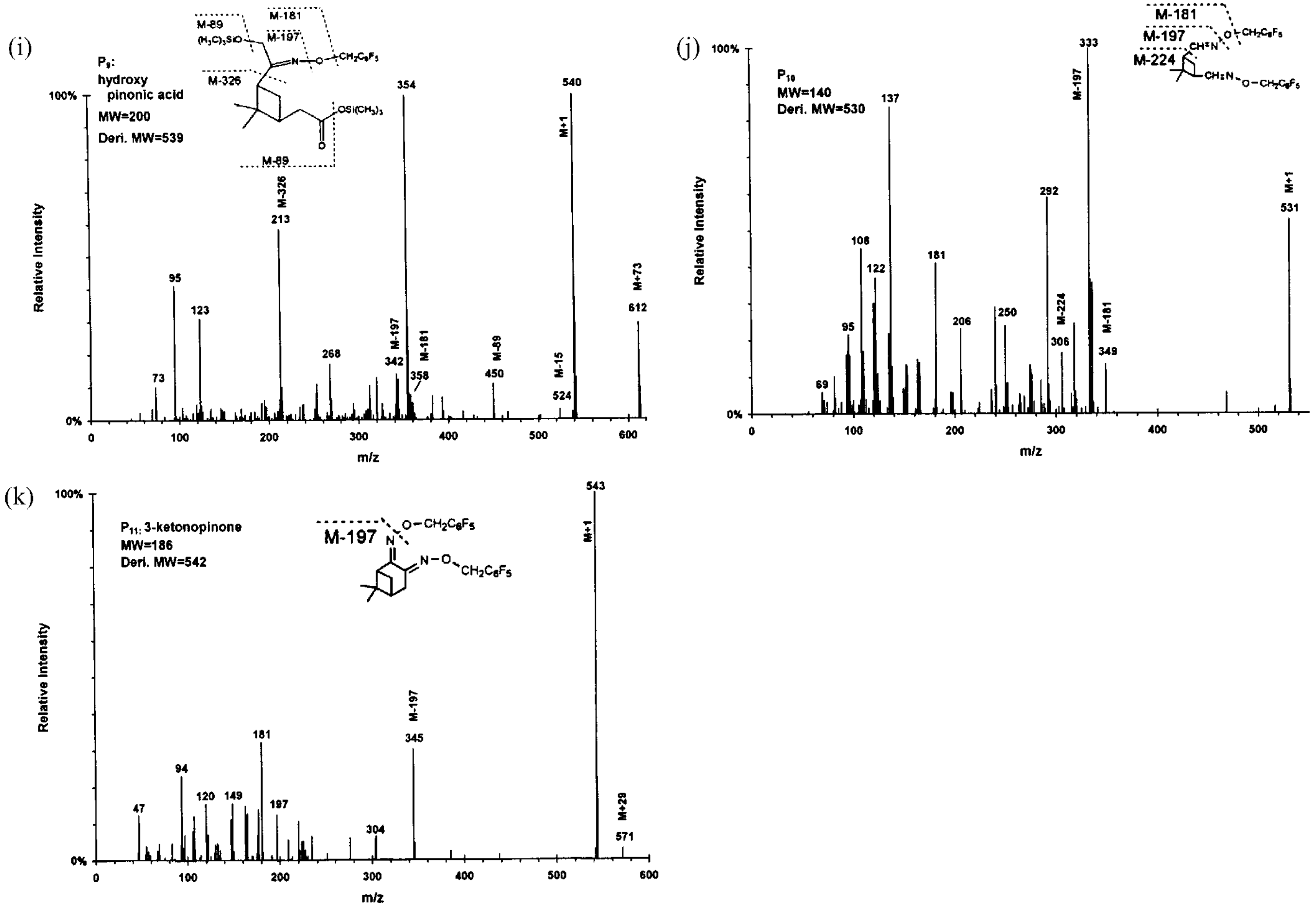
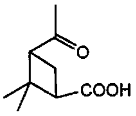
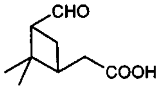


Figure 2. (Continued).



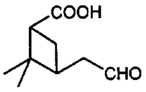
norpinonic acid

(3-acetyl-2,2-dimethyl cyclobutylmethanoic acid)



pinalic-4-acid

(2,2-dimethyl-3-formyl cyclobutylethanoic acid)



pinalic-3-acid

(2,2-dimethyl-3-formylmethyl cyclobutylmethanoic acid)

Further differentiation among the three isomers is impossible on the basis of CI and EI mass spectra. Figure 2-P_6 shows ion fragment patters using pinalic-4-acid as an example. Compound P_7 is identified as cis-pinonic acid, and the identification has been confirmed by comparison with an authentic standard. The CI mass spectrum of its derivative is shown in Figure 2-P_7. Compound P_8 is tentatively identified as hydroxy norpinonic acid, with a MW of 525 for its derivative (Figure 2-P_8). Compound P_9 is tentatively identified as hydroxy pinonic acid, with a MW of 539 for its derivative (Figure 2-P_9).

Some of the products observed here have been reported in previous studies. Nopinone has long been identified as a major product in the β-pinene/O_3 reaction (Hull, 1981; Hatakeyama *et al.*, 1989; Grosjean *et al.*, 1993, Hakola *et al.*, 1994). Using GC/MS and nuclear magnetic resonance (NMR) analyses, Hull also positively identified 3-hydroxy-pina ketone and 3-oxo-pina ketone and had indirect evidence for the formation of 1-hydroxy-pina ketone. Products that are reported here for the first time include pinic acid, norpinic acid, 2,2,-dimethyl-3-formyl-cyclobutyl methanoic acid, norpinonic acid and its isomers, pinonic acid, hydroxy norpinonic acid, hydroxy pinonic acid, and 2,2-dimethyl-cyclobutane-1,3-dicarboxaldehyde.

3.2. PRODUCTS FROM OZONE OXIDATION OF SABINENE

Carbonyl bearing products of the sabinene/O_3 reaction are shown in Figure 3(a), and OH/COOH bearing products are shown in Figure 3(b). Table V lists the MWs and chemical structures of these products. Most products are analogous to those identified in the β-pinene/O_3 reaction, and their methane CI mass spectra are similar to those in the β-pinene/O_3 reaction. The CI mass spectra are given only for the products unique in the sabinene/O_3 reaction (Figure 4). Interested readers can get from us the mass spectra data for those analogous products.

Among the products, compound S_1, S_2, and S_3 contain only OH/COOH groups (type 2 compounds). Compound S_1 is tentatively identified as norsabinic acid on the basis of that it shows a MW of 316 for its derivative, and elutes at an earlier retention time than that of norpinic acid. The CI spectrum of compound S_2 indicates a MW of 330 for its TMS derivative. S_2 elutes from the GC column earlier than pinic acid. It is tentatively identified as sabinic acid, the analogue of pinic acid derived from sabinene. Compound S_3 is pinic acid, confirmed by authentic standard. The

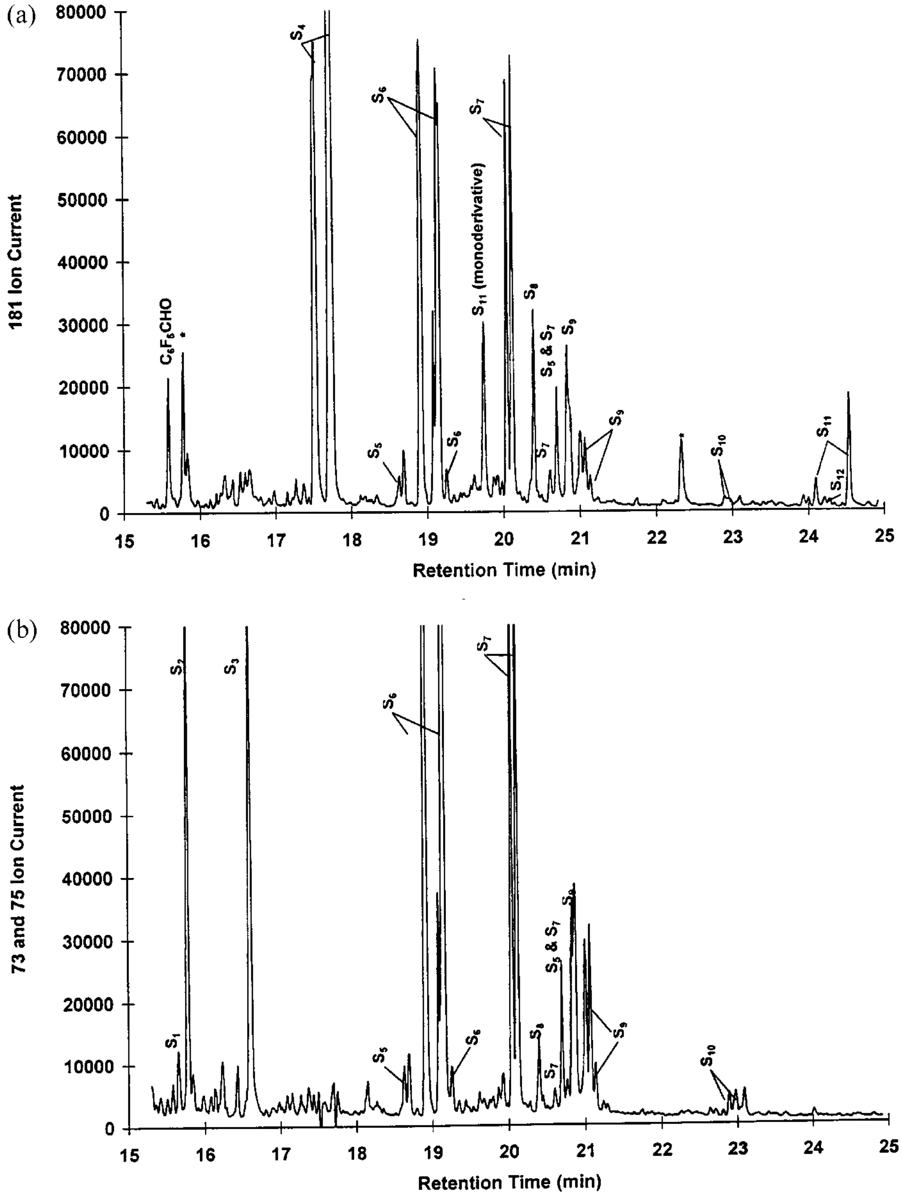


Figure 3. Chromatogram of products from sabinene/O_3 reaction. See Table V for peak identification. Top: Products containing carbonyl groups. Bottom: Products containing OH/COOH groups.

Table V. Products from ozone oxidation of sabinene

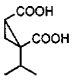
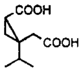
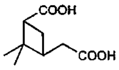
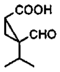
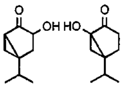
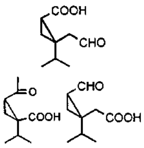
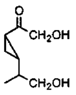
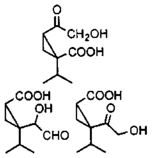
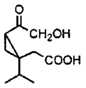
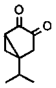
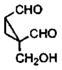
Name	Structure	Pseudo-molecular ions in CI mass spectrum	
S_1: $C_8H_{12}O_4$ MW = 172 deri. MW = 316		M+73: 389 M-15: 301 M-117: 199	M+1: 317 M-89: 227
S_2: $C_9H_{14}O_4$ sabinic acid MW = 186 deri. MW = 330		M+73: 403 M-15: 315 M-117: 225	M+1: 331 M-89: 241
S_3: $C_9H_{14}O_4$ pinic acid MW = 186 deri. MW = 330		M+73: 403 M-15: 315	M+1: 331 M-89: 241
S_4: $C_9H_{14}O$ sabina ketone MW = 138 deri. MW = 333		M+181: 514 M+1: 334 M-197: 136	M+29: 362 M-181: 152
S_5: $C_8H_{12}O_3$ 2-(2-isopropyl)-2-formyl-cyclopropyl-methanoic acid MW = 156 deri. MW = 423		M+73: 496 M-15: 408 M-181: 242	M+1: 424 M-89: 334 M-197: 226
S_6: $C_9H_{14}O_2$ hydroxy sabina ketones MW = 154 deri. MW = 421		M+181: 602 M-15: 406 M-197: 224	M+1: 422 M-89: 332 M-212: 210
S_7: $C_9H_{14}O_3$ norsabinonic acid and its isomers MW = 170 deri. MW = 437		M+197: 634 M+73: 510 M-15: 422 M-197: 240	M+181: 618 M+1: 438 M-89: 348
S_8: $C_8H_{12}O_3$ MW = 156 deri. MW = 495	e.g. 	M+89: 584 M+29: 524 M-89: 406 M-197: 298	M+1: 496 M-15: 480 M-147: 348

Table V. (Continued)

Name	Structure	Pseudo-molecular ions in CI mass spectrum	
S_9: $C_9H_{14}O_4$ hydroxy norsabinonic acid MW = 186 deri. MW = 525		M+73: 598 M-15: 510 M-197: 328	M+1: 526 M-89: 436
S_{10}: $C_{10}H_{16}O_4$ MW = 200 deri. MW = 539	e.g. 	M+73: 612 M-15: 524 M-181: 358	M+1: 540 M-89: 450 M-197: 342
S_{11}: $C_9H_{12}O_2$ 3-oxo-sabina ketone MW = 152 deri. MW = 542		M+29: 571 M-197: 345	M+1: 543
S_{12}: $C_6H_8O_3$ MW = 128 deri. MW = 590	e.g. 	EI spectrum M: 590 M-181: 409	 M-15: 575 M-197: 393

observation of pinic acid as a product in the sabinene/O_3 reaction is also reported by Glasius *et al.* (1998). It is not likely that pinic acid is a residue resulting from the previous chamber experiment, which was a β-pinene/O_3 experiment. Between chamber experiments, clean air of more than 15 times the bag volume passes through the reactor. More experiments are needed to verify this observation.

Compounds S_4 and S_{11} are found to contain only carbonyl groups (type 1 compounds), indicated by their presence in Figure 3(a) and absence in Figure 3(b). Both EI and CI spectra indicate a MW of 333 for compound S_4. It is tentatively identified as sabina ketone. This product is identified as a major product by Hakola *et al.* (1994). Compound S_{11} is tentatively identified as 3-oxo-sabina ketone. The mono-derivative of this diketone is also present.

Compounds S_5, S_6, S_7, S_8, S_9, S_{10}, and S_{12} have both carbonyl and OH/COOH groups (type 3 compounds), indicated by their presence in both Figure 3(a, b). Compound S_5 is tentatively identified as 2-(2-isopropyl)-2-formyl-cyclopropylmethanoic acid, as its CI spectrum shows a MW of 423 for its PFBHA and TMS derivative. Three peaks are ascribed to S_6, and their CI spectra indicate a MW of 421. S_6 is therefore tentatively identified as hydroxy sabina ketones (3-hydroxy and 1-hydroxy sabina ketone). Four peaks are assigned to S_7, which has a MW of

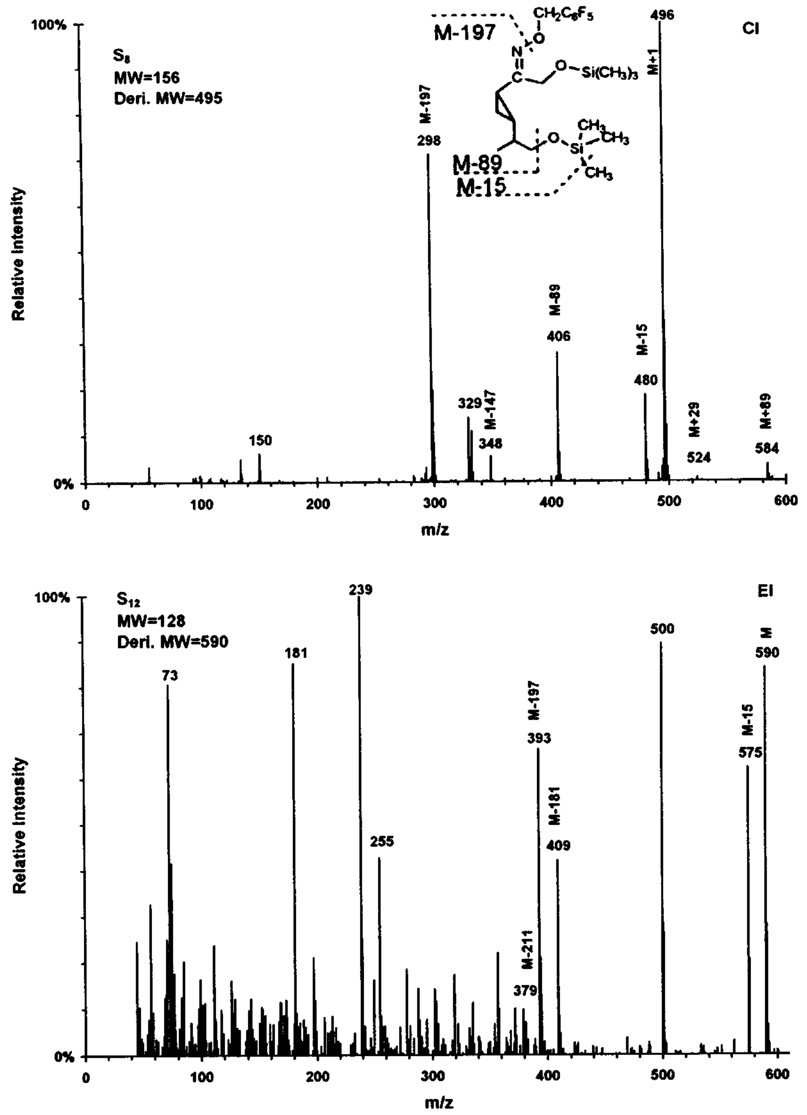


Figure 4. Mass spectra for the derivatives of two products (S_8 and S_{12}) from ozone oxidation of sabinene.

437. Similar to P_7 peaks in the β-pinene/O_3 samples, S_7 could be two of the three isomers listed in Table V. Further differentiation is not possible based on the mass spectra data. Peak S_8 shows a MW of 495 (Figure 4-S_8). Table V lists one of the possible candidates that matches the MW and functional group types. Three peaks, with a MW of 525 determined from their CI mass spectra, are assigned to S_9. Three of all possible structures are listed in Table V. S_{10} is determined to have a MW of 539 for its derivatized form. Two peaks are ascribed to compound S_{12}, with a MW

of 590 for its derivatized forms. One EI spectrum is given in Figure 4-S_{12}. Their CI spectra are weak, but the protonated molecular ion is present. One postulated structure is listed in Table V.

A comparison of the products from β-pinene/O_3 and sabinene/O_3 reveals that there are nine analogous product pairs in the two reaction systems: Norpinic acid/norsabinic acid, pinic acid/sabinic acid, nopinone/sabina ketone, P_5/S_5, hydroxy pina ketones/hydroxy sabina ketones, P_6/S_7, P_8/S_9, P_9/S_{10}, and 3-oxo-pina ketone/3-oxo-sabina ketone (Tables IV and V). These analogous products suggest that they are derived from a common moiety between the two parent reactants, i.e., an external unsaturated bond to the six-member ring. The sabinene/O_3 reaction also produces two unique products (S_8 and S_{12}), correspondents of which are not observed in the β-pinene/O_3 reaction.

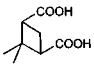
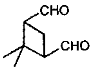
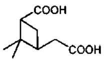
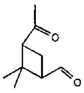
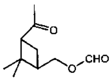
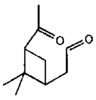
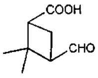
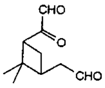
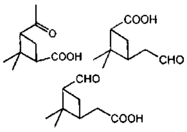
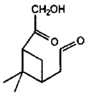
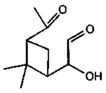
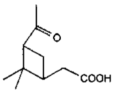
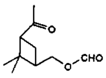
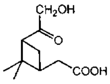
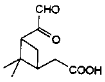
3.3. PRODUCTS FROM OZONE OXIDATION OF α-PINENE

Identification of ozone oxidation products of α-pinene, based on a collection of $\sim$0.36 m^3 reactor air in an impinger, has been described by Yu *et al.* (1998). The collection of a larger air volume (1.5 m^3) by the denuder/filter system in this work allows detection of six additional minor products. For completeness, Table VI shows the structures of all the identified products. The six additional products identified include norpinic acid (A_1), (2,2-dimethyl-3-acetyl)-cyclobutyl formate (A_3), hydroxy pinonic acid (A_7), A_{11}, A_{13}, and A_{14} (see Table VI). Figures 5(a, b) are the GC chromatograms for carbonyl and COOH/OH bearing products, respectively. Some of the products in the β-pinene/O_3 reaction are also observed in the β-pinene/O_3 system, apparently as a result of the common moieties shared by α-pinene and β-pinene. Unique products in the α-pinene/O_3 reaction include A_3, and A_9–A_{14}. Their CI spectra are displayed in Figure 6.

The tentative identifications of (2,2-dimethyl-3-acetyl)-cyclobutyl formate (A_3), norpinonaldehyde (A_9), pinonaldehyde (A_{10}), and hydroxy pinonaldehydes (A_{12}) are based on their mass spectra and reasonable postulation of the gas-phase α-pinene/O_3 reaction mechanism (Yu *et al.*, 1998). Possible structures for A_{11}, A_{13}, and A_{14} are suggested based on their mass spectra (Table VI).

A number of recent product studies of the α-pinene/O_3 reaction have also revealed some of the products observed in this work (Hoffmann *et al.*, 1998; Glasius *et al.*, 1998, 1999; Jang and Kamens, 1998). Using HPLC/atmospheric pressure chemical ionization (APCI) mass spectrometry, Hoffmann *et al.* (1998) reported the observation of pinic acid, norpinic acid, pinonic acid, and evidence for an adduct of pinic acid and norpinic acid. Such a binary diacid adduct, if existing, would likely dissociate when undergoing the heating treatment (70 °C for 2.5 hrs) used for the silylation derivatization. Glasius *et al.* (1999), using HPLC/ electrospray ionization and APCI mass spectrometry, reported observation of pinonic acid, pinic acid, norpinic acid, hydroxy pinonic acid, and pinalic-4-acid. Jang and Kamens (1998), using derivatization techniques and GC/MS detection similar to this work,

Table VI. Products from ozone oxidation of α-pinene

Product	Structure	Product	Structure
A_1: $C_8H_{12}O_4$ norpinic acid MW = 172 deri. MW = 316		A_8: $C_8H_{12}O_2$ 2,2-dimethyl-cyclobutyl-1,3-dicarboxaldehyde MW = 140	
A_2: $C_9H_{14}O_4$ pinic acid MW = 186 deri. MW = 330		A_9: $C_9H_{14}O_2$ norpinonaldehyde MW = 154 deri. MW = 544	
A_3: $C_{10}H_{16}O_3$ (2,2-dimethyl-3-acetyl)-cyclobutyl formate MW = 184 deri. MW = 379		A_{10}: $C_{10}H_{16}O_2$ pinonaldehyde MW = 168 deri. MW = 558	
A_4: $C_8H_{12}O_3$ 2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid MW = 156 deri. MW = 423		A_{11}: $C_{10}H_{14}O_3$ MW = 182 deri. MW = 572	
A_5: $C_9H_{14}O_3$ norpinonic acid and isomers MW = 170 deri. MW = 437		A_{12}: $C_{10}H_{16}O_3$ hydroxy pinonaldehydes MW = 184 deri. MW = 646	 
A_6: $C_{10}H_{16}O_3$ pinonic acid MW = 184 deri. MW = 451		A_{13} MW = 198 deri. MW = 588	e.g. 
A_7: hydroxy pinonic acid MW = 200 deri. MW = 539		A_{14}: $C_{10}H_{14}O_3$ MW = 198 deri. MW = 660	e.g. 

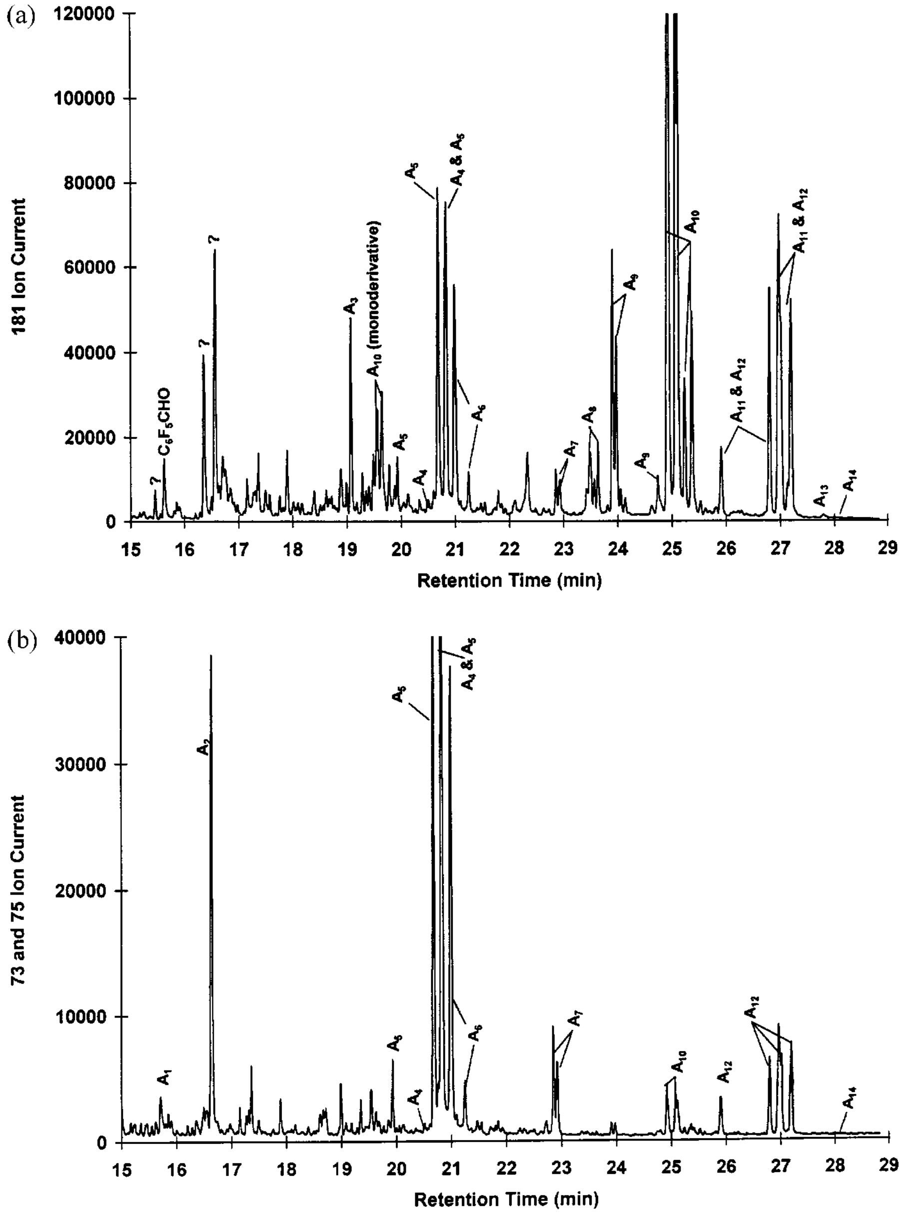


Figure 5. Chromatogram of products from α-pinene/O_3 reaction. See Table VI for peak identification. Top: Products containing carbonyl groups. Bottom: Products containing OH/COOH groups.

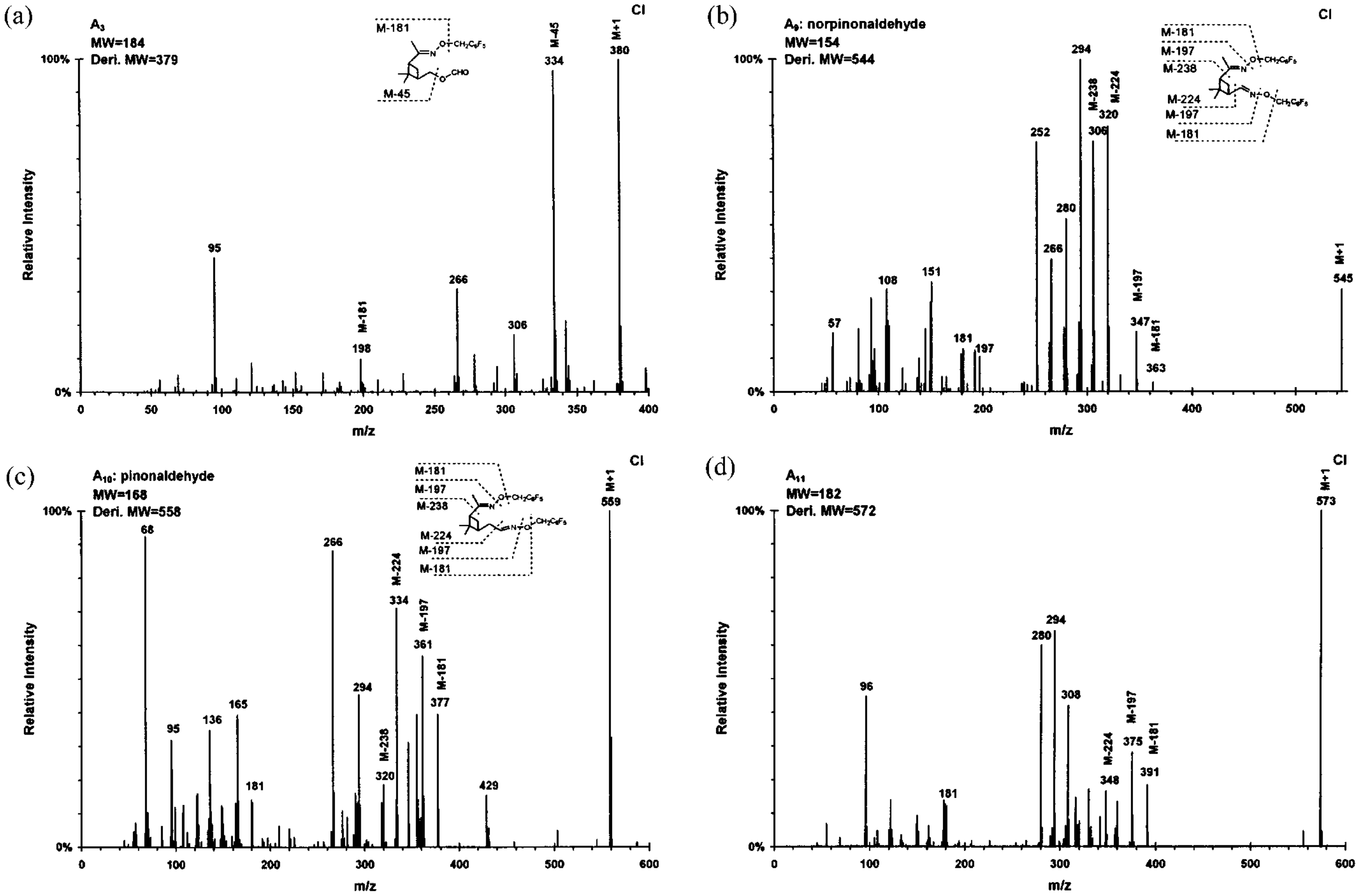


Figure 6. Mass spectra for the derivatives of products from ozone oxidation of α-pinene.

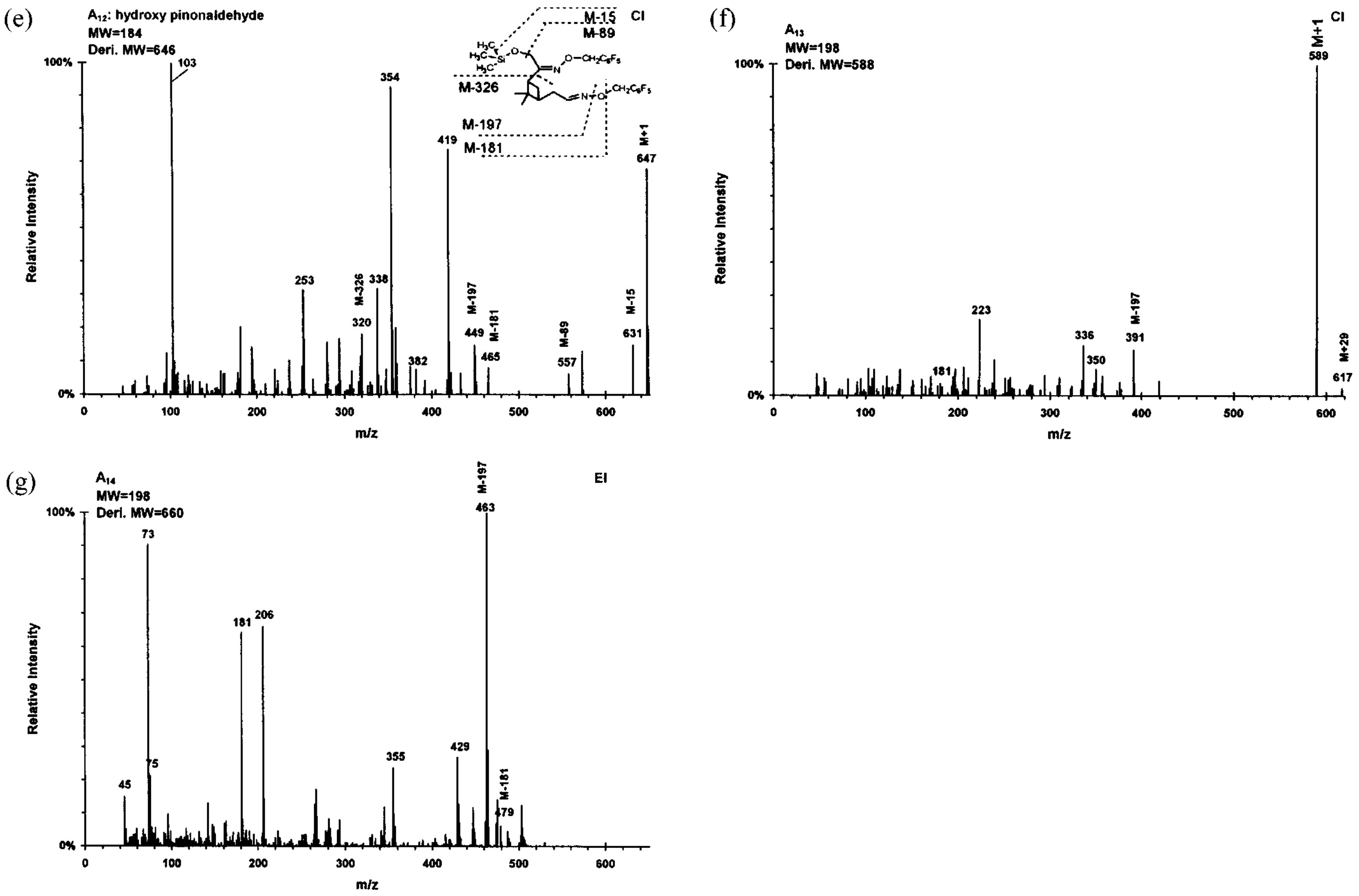


Figure 6. (Continued).

tentatively identified norpinic acid, pinic acid, norpinonic acid, pinonic acid, 2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid, norpinonaldehyde, pinonaldehyde, pinalic-3-acid, hydroxy pinonic acid, and A_{14}. Compounds A_3, A_{11} and A_{13} are reported here for the first time.

3.4. PRODUCTS FROM OZONE OXIDATION OF Δ^3-CARENE

Identification of ozone oxidation products of Δ^3-carene based on impinger samples has been described by Yu *et al.* (1998). Using the denuder/filter pack collection system, we have identified additional products in small yields. Figures 7(a, b) are the GC chromatograms of the derivatized products in a denuder sample. Table VII lists the structures of these products and the pseudo-molecular ions in their CI mass spectra, which are used to determine MWs. Due to lack of authentic standards, all the products are tentatively identified on the basis of their mass spectra and possible reaction mechanism. Many of the products in the Δ^3-carene/O_3 reaction are analogous in structure to those in the α-pinene/O_3 reaction. The CI mass spectra of the products, which do not have analogous products in the α-pinene/O_3 reaction, are given in Figure 8. The CI mass spectra for C_7 and C_8 have been shown in the previous paper (Yu *et al.*, 1998).

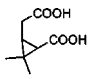
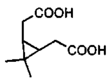
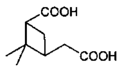
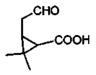
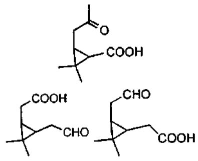
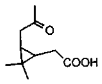
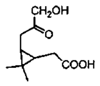
Additional products identified in the denuder sample include nor-caric acid (C_1), pinic acid (C_3), C_4, C_5, and C_{10}. For C_4, C_5, and C_{10}, we are not currently able to suggest possible chemical structures, so only their MW and the presence of functional group types are given in Table VII. These three products do not have corresponding analogues in the α-pinene/O_3 reaction. On the other hand, four products, A_3, A_{11}, A_{13}, and A_{14}, are found unique to the α-pinene/O_3 reaction. This is not unexpected as minor reaction pathways may take place at locations other than the C=C bond.

The observation of pinic acid in the Δ^3-carene/O_3 reaction is not expected. Glasius *et al.* (1998) also observed trace amount of pinic acid in their Δ^3-carene/O_3 reaction systems.

4. Product Yields

Yields of the above-identified products have been determined or estimated. For products with standards, the calibration factor, extraction recovery, and collection efficiency have been determined using the standards. For products that do not have available authentic standards, their yields are estimated using the calibration factor, and the recovery and collection efficiency of surrogate compounds. The surrogate compounds are chosen to have the same type of functional groups and approximate carbon numbers as the products that the surrogates represent. Table VIII lists the available standards and the products for which the standards serve as surrogates. For example, pinic acid serves as the surrogate for norpinic acid, 3-caric acid, nor-3-caric acid, sabinic acid, and norsabinic acid. Carbonyl bearing products (type 1

Table VII. Products from ozone oxidation of Δ^3-carene

Product	Structure	Pseudo-molecular ions in CI mass spectrum	
C_1: $C_8H_{12}O_4$ nor-3-caric acid MW = 172 deri. MW = 316		M+1: 317 M-89: 227	M-15: 301 M-117: 199
C_2: $C_9H_{14}O_4$ 3-caric acid MW = 186 deri. MW = 330		M+147: 477 M+29: 359 M-15: 315 M-117: 213	M+73: 403 M+1: 331 M-89: 241
C_3: $C_9H_{14}O_4$ pinic acid MW = 186 deri. MW = 330		M+73: 403 M-15: 315 M-117: 213	M+1: 331 M-89: 241
C_4: MW = 118 deri. MW = 457	One carbonyl and two OH/COOH groups	M+181: 638 M-15: 442 M-117: 340	M+1: 458 M-89: 368 M-197: 260
C_5: MW = 142 deri. MW = 337	One carbonyl group, no OH/COOH groups	M+181: 518 M-17: 320	M+1: 338 M-197: 140
C_6: $C_8H_{12}O_2$ MW = 140 deri. MW = 423		M+1: 424 M-197: 226	M-89: 334
C_7: $C_9H_{14}O_3$ 3-norcaronic acid and isomers MW = 170 deri. MW = 437		M+73: 510 M-89: 348 M-197: 240	M+1: 437 M-181: 256
C_8: $C_{10}H_{16}O_3$ 3-caronic acid MW = 184 deri. MW = 451		M+73: 524 M-89: 362 M-197: 254 M-211: 240	M+1: 452 M-181: 270 M-197: 254
C_9: $C_{10}H_{16}O_3$ hydroxy 3-caronic acid MW = 184 deri. MW = 539	e.g. 	M+1: 540 M-197: 342	M-89: 450
C_{10}: MW = 128 deri. MW = 518	Two carbonyl groups, no OH/COOH groups	M+1: 519 M-197: 321	M-181: 337 M-224: 294

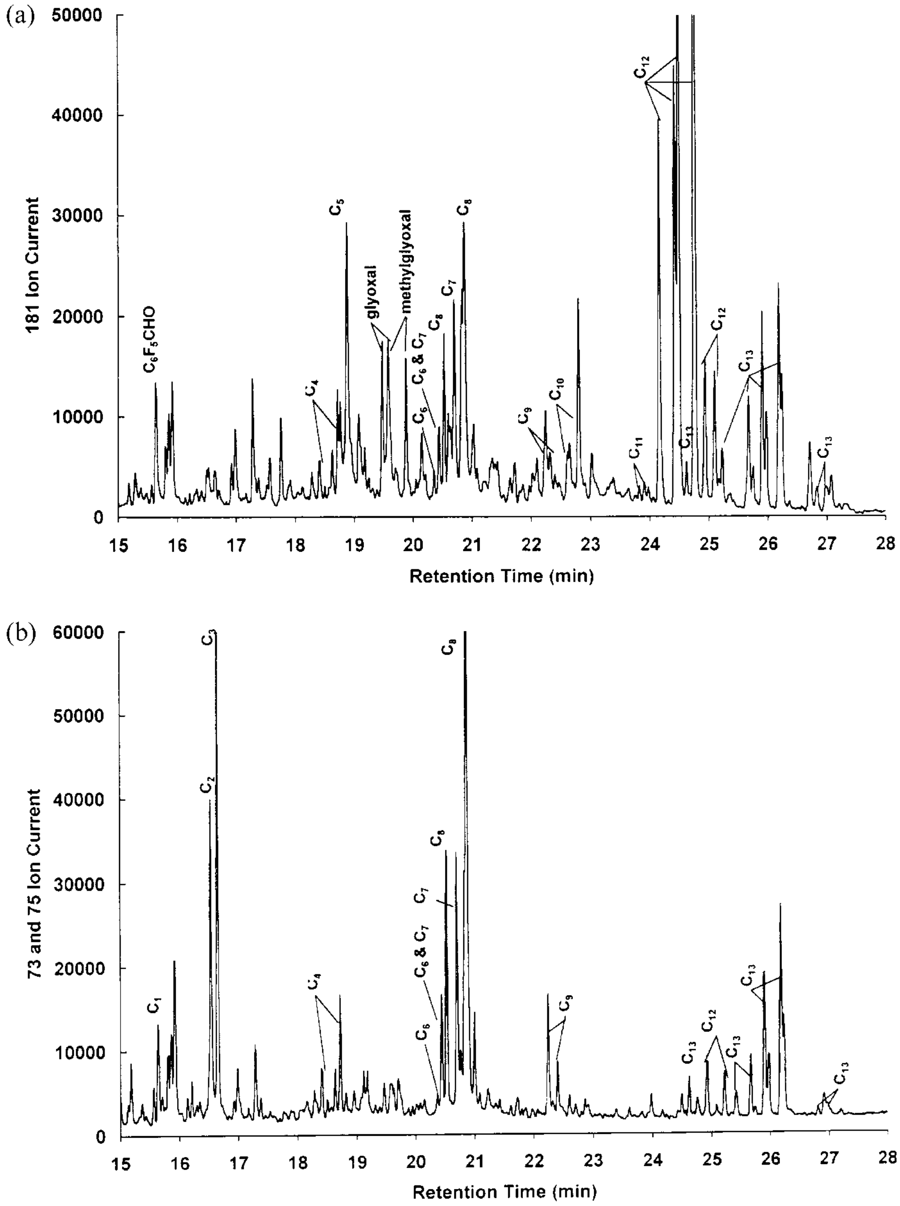


Figure 7. Chromatogram of products from Δ^3-carene/O_3 reaction. See Table VII for peak identification. Top: Products containing carbonyl groups. Bottom: Products containing OH/COOH groups.

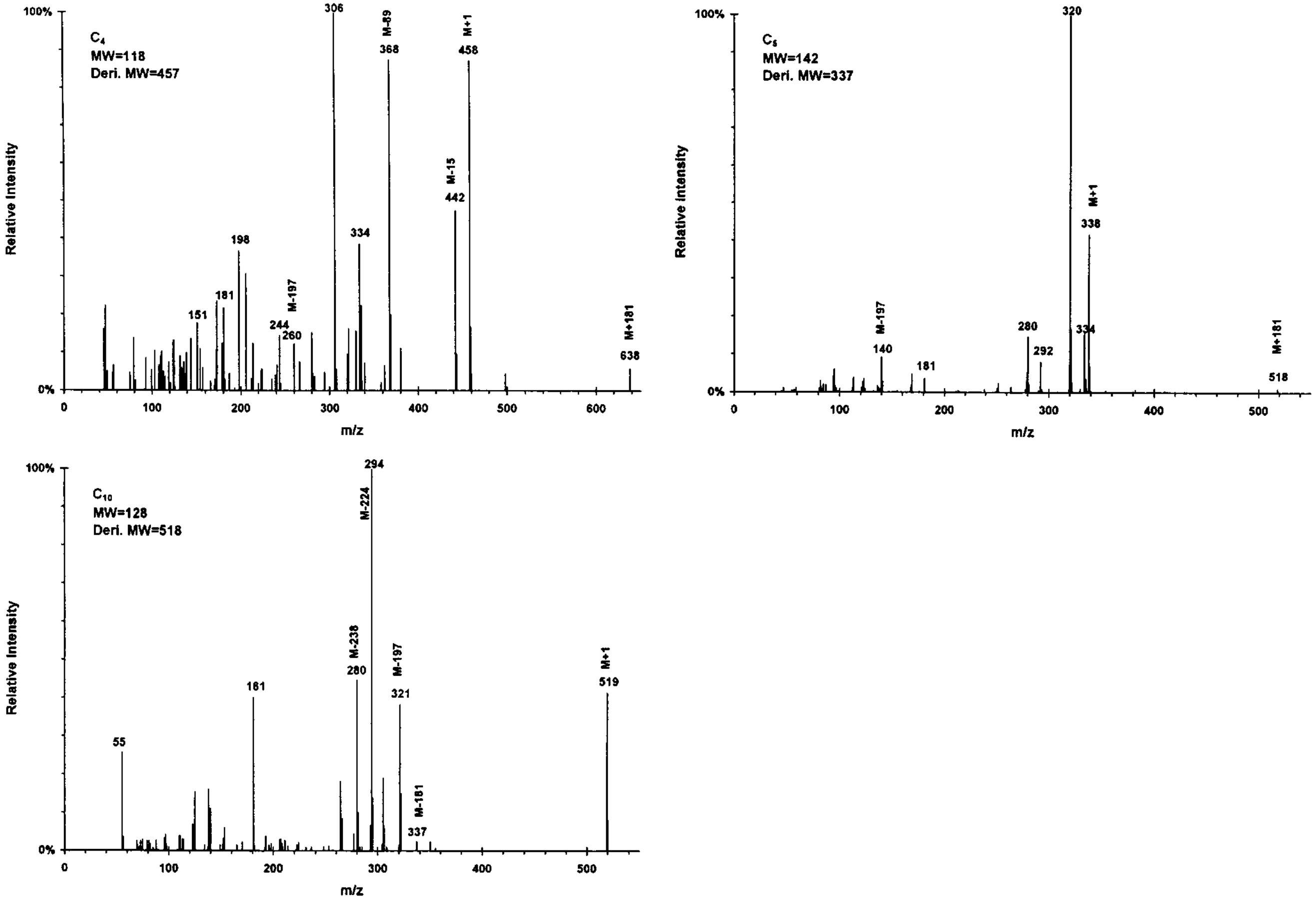


Figure 8. Methane CI mass spectra for the derivatives of products from ozone oxidation of Δ^3-carene.

Table VIII. Products and their surrogates for quantification

Standard	Products surrogated for			
	β-Pinene/O_3	Sabinene/O_3	α-Pinene/O_3	Δ^3-Carene/O_3
Pinic acid	Norpinic acid	Sabinic acid, norsabinic acid	Norpinic acid	3-Carid acid, nor-3-caric acid
Pinonic acid	P_5, norpinonic acid and its isomers, hydroxy norpinonic acid, hydroxy pinonic acid	Sabinonic acid, norsabinoic acid and its isomers, S_8, S_9, S_{10}	A_4, norpinonic acid and its isomers, hydroxy pinonic acid,	3-Caronic acid, nor-3-caronic acid and its isomers, C_6, C_9
2-Hydroxy-cyclohexanone	Hydroxy pina ketones	Hydroxy sabina ketones		
5-Methyl-1,3-cyclohexanedione	P_{10}, 3-oxo-pina ketone	3-Oxo-sabina ketone, S_{12}	Pinonaldehyde, norpinonaldehyde, A_8, A_{11}, hydroxy pinonaldehydes, A_{13}, A_{14}	C_{10}, norcaronaldehyde, caronaldehyde, hydroxy caronaldehydes
Nopinone		Sabine ketone	A_3	C_5

compounds) are quantified using the *m/z* 181 ion, products bearing COOH/OH groups (type 2 compounds) are quantified using the *m/z* 73 and 75 ions, and for those products that contain both carbonyl and COOH/OH groups (type 3 compounds), the sum of three ions at *m/z* 181, 73 and 75 is used for their quantification. The selection of surrogates on the basis of functional group types is justified by the use of the above functional group specific ions for quantification. The estimated calibration factors have a ∼ ±30% uncertainty. The other sources that contribute to the uncertainty associated with product yields include uncertainties for collection efficiency (∼ ±4%), extraction efficiency (∼ ±15%) and sample volume (±5%). After considering all contributing sources, the uncertainty associated with product yields is estimated to be ∼ ±50%.

Our calculation of gaseous product yields ignores wall loss processes, as we estimate that the loss of an oxygenated product resulting from wall loss processes is likely less than 15% at 300 min after its formation. Grosjean (1985) measured the wall loss rates for five oxygenated species, biacetyl, pyruvic acid, o-cresol, benzaldehyde, and benzoic acid in a Teflon chamber with a S/V of 3.8 m^{-1}. The first three compounds had an unmeasurable wall loss rate while benzaldehyde and benzoic acid had wall loss rates of 3.4×10^{-4} and 10.8×10^{-4} min^{-1}, respectively. Hallquist *et al.* (1997) measured the wall loss rates for pinonaldehyde and caronaldehyde to be $(2.4–4.2) \times 10^{-3}$ min^{-1} in a borosilica glass reactor with a S/V of 14.3 m^{-1}. If one assumes wall loss processes are similar on borosilica glass and Teflon surfaces, one could calculate that the two dicarbonyls have a wall loss rate of $(3–5) \times 10^{-4}$ min^{-1}, comparable to that for benzoic acid (5×10^{-4} min^{-1}), in the present Teflon reactor with a S/V of 1.8 m^{-1}. Using the wall loss rate for benzoic acid, which has the highest wall loss rate among all the tested oxygenated species, we estimate that about 86% of an oxygenated product remains in the gas phase at 300 min after its formation, if we assume that wall loss is the only loss process. A more detailed study of gas-phase product yields needs experimentally determined wall loss rates for each product, which unfortunately can not be readily accomplished as many products lack commercially available standards.

The organic aerosol mass generated in each experiment was obtained from the aerosol volume measured by SEMS/CNC and assuming a SOA density of 1 g cm^{-3}. The SOA yield (Y) was then calculated by

$$\mathrm{Y} = \frac{\Delta \mathrm{M}_o}{\Delta \mathrm{HC}}, \tag{1}$$

where $\Delta \mathrm{M}_o$ is the organic aerosol mass concentration (μg m^{-3}) produced for a given amount of hydrocarbon reacted, ΔHC (μg m^{-3}). The estimated uncertainty in the measured SOA yield is roughly ±12%, with SOA density uncertainty assumed to be ±10%.

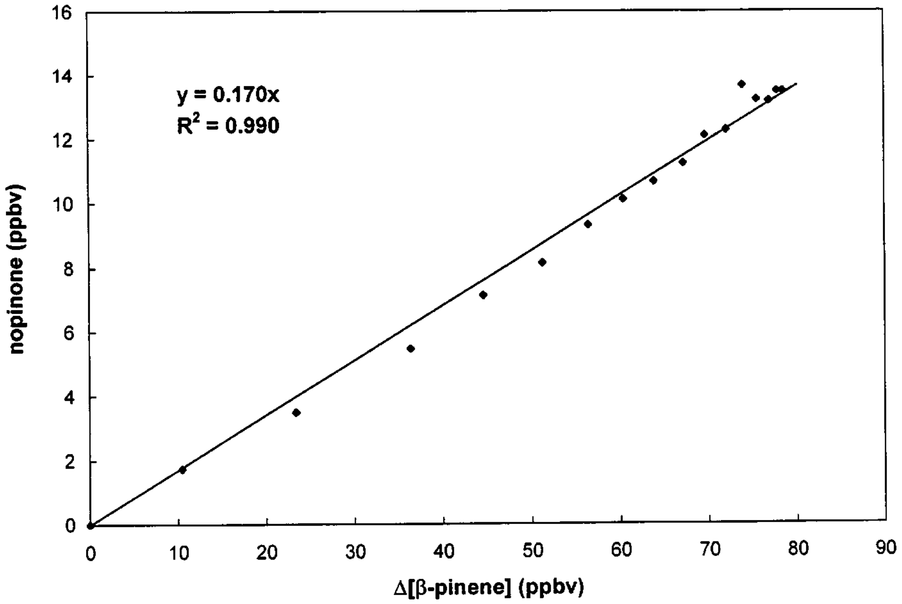


Figure 9. Amount of nopinone formed versus the amount of β-pinene reacted.

4.1. β-PINENE

Table IX shows yields of individual products in gas and aerosol phases, as well as the total yields in two β-pinene/O_3 experiments. The yield of nopinone in the gas-phase is determined from measurements made by an on-line GC/FID, as GC/FID provides more accurate and frequent measurements of nopinone. As an example, Figure 9 shows the amount of nopinone formed against the amount of β-pinene reacted for the experiment carried out on 11 June 1998 (side B). The gas-phase yield of nopinone was determined to be 17.0% and 15.8% in the 6/11/98b and 6/17/98b experiments, respectively. Nopinone resides almost exclusively in the gas phase; trace amounts were detected in the filter samples. Previously reported nopinone yields vary from 22% (Grosjean *et al.*, 1993) and 23 ± 5% (Hakola *et al.*, 1994) to 40 ± 2% (Hatakeyama *et al.*, 1989). The much higher nopinone yield in the study by Hatakeyama *et al.* (1989) is possibly due to the presence of other carbonyl products that were reported as nopinone, as their measurement of nopinone was based on FTIR absorption spectroscopy at the 1740 cm^{-1} –C=O stretch frequency.

Only one study in the literature (Hull, 1981) reported yields for individual products other than nopinone in the β-pinene/O_3 reaction. In this study, Hull estimated the total molar yields of three major products: Nopinone (10%), 3-hydroxy-pina-ketone (28%), and 3-oxo-pina-ketone (7%). The total molar yield for 3-hydroxy-pina ketone in the present work is estimated to be 7.3% and 9.0% in the two experiments, lower than Hull's result. Our yield for 3-oxo-pina-ketone is estimated to be 1.8% and 7.7%. In his study, Hull used high mixing ratios for *beta-*

Table IX. Gaseous and particulate product yields in the β-pinene/O_3 reaction

	Molar yield (%)						Aerosol yield by mass (%)	
	Gas		Aerosol		Total			
Experiment data	6/11/98b	6/17/98b	6/11/98b	6/17/98b	6/11/98b	6/17/98b	6/11/98b	6/17/98b
Pinic acid	1.7	2.5	0.91	1.2	2.6	3.7	1.2	1.6
Norpinic acid	0.23	0.17	0.11	0.09	0.35	0.27	0.17	0.12
Pinonic acid	0.41	0.56	0.10	0.19	0.52	0.74	0.14	0.25
Norpinonic acid and isomer	4.6	14.3	1.3	2.2	5.9	16.5	1.7	2.7
Hydroxy pine ketones	6.6	7.9	0.66	1.1	7.3	9.0	0.74	1.3
3-Oxo-pina-ketone	1.8	7.6	0.02	0.11	1.8	7.7	0.02	0.12
2,2-Dimethyl-cyclobutane-1,3-dicarboxaldehyde	0.35	0.29	ND[a]	ND	0.35	0.29	ND	ND
Nopinone	17.0	15.8	trace	trace	17.0	15.8	trace	trace
Hydroxy norpinonic acid	0.58	0.98	0.10	0.24	0.68	1.2	0.14	0.33
Hydroxy pinonic acid	0.26	0.16	0.17	0.15	0.43	0.31	0.25	0.20
Total molar yield	33.5	50.3	3.4	5.3	36.9	55.6	4.4	6.6
Carbon-based total yield					34.2	50.1		
Aerosol yield measured by SEMS and CNC							4.5	8.3

[a] Not detectable.

pinene (275 to 440 ppmv) and ozone (179 to 270 ppmv), and no OH scavenger. The very different reaction conditions may account for the different product yields.

The identified products account for 34% and 50% of the reacted β-pinene carbon mass in the 6/11/98b and 6/17/98b experiments, respectively. Products with a yield exceeding $>1\%$ include nopinone (15.8–17.0%), hydroxy pina ketones (7.3–9.0%), 3-oxo-pina-ketone (1.8–7.7%), norpinonic acid and its isomers (5.9–16.5%), and pinic acid (2.6–3.7%). The identified products are estimated to account for 98% and 83% of the organic aerosol mass formed in the two β-pinene/O_3 experiments. Norpinonic acid and its isomers, pinic acid and hydroxy pina ketones are SOA components that contribute to more than 10% of the organic aerosol mass.

The 6/17/98b experiment has a much higher percentage of reacted β-pinene accounted for by the identified products than the 6/11/98b experiment, as two major products, norpinonic acid and its isomers and 3-oxo-pina-ketone, were observed to have much higher gas-phase yields in the 6/17/98b experiment (Table IX). The two β-pinene/O_3 experiments were conducted under different initial conditions, i.e., ozone was present in an excess amount in the 6/11/98b experiment whereas β-pinene is in excess in the 6/17/98b experiment (Table I). The variation between the two experiments can not be accounted for by measurement error alone. It is possible the different initial reaction conditions are responsible for the variation, but a satisfactory explanation is not possible without further experiments designed to systematically examine the effects of different reaction conditions on product yields.

The functional group distribution of SOA components from the β-pinene/O_3 experiments is comparable to results obtained by Palen *et al.* (1992) using Fourier transform infrared spectrometry (FTIR). Palen *et al.* analyzed aerosol samples generated from an experiment with 8 ppmv O_3 and 14.5 ppmv β-pinene. Their results indicated that an average aerosol-phase product molecule contained one ketone group, 0.7 alcohol groups, and 0.4 carboxylic groups. For the 6/17/98 β-pinene/O_3 experiment where excessive β-pinene was used, our GC/MS analysis showed that the average aerosol molecule contained about one ketone group, 0.2 alcohol groups, and 0.8 carboxylic groups.

4.2. SABINENE

Table X shows yields of individual products in the gas and aerosol phases, as well as the total yields of both phases in the sabinene/O_3 experiment. Identified products in both the gas and aerosol phases account for 57% of the reacted sabinene carbon mass. Products with a molar yield exceeding 1% include sabina ketone (47%), hydroxy sabina ketone (7%), norsabinonic acid and its isomers (5%), pinic acid (1%), and sabinic acid (1%).

All the products added together account for 100% of the organic aerosol mass formed. The 100% yield is rather fortuitous, and it is associated with an uncertainty factor resulting from the approximations made for response factors and SOA

Table X. Gaseous and particulate product yields in the sabinene/O_3 reaction

Product	Molar yield (%)			Aerosol yield by mass (%)
	Gas	Aerosol	Total	
Pinic acid	1.1	0.29	1.4	0.39
Sabinic acid	0.80	0.39	1.2	0.53
Norsabinic acid	0.18	0.07	0.25	0.09
Norsabinonic acid and its isomers	3.6	1.1	4.7	1.4
Hydroxy-sabina-ketones	6.6	0.43	7.0	0.53
3-Oxo-sabina-ketone	0.50	0.01	0.51	0.01
S_5[a]	0.15	0.11	0.26	0.13
Sabine ketone	46.2	0.43	46.6	0.43
S_8[a]	0.54	ND	0.54	ND
S_9[a]	0.75	ND	0.75	ND
S_{10}[a]	0.12	0.02	0.14	0.03
Total molar yield	60.5	2.9	63.4	3.5
Carbon-based total yield			57.0	
Aerosol yield measured by SEMS and CNC				3.5

[a] See Table V for possible candidate structures.

density. Aerosol components that make up more than 10% of the aerosol mass are norsabinoic acid and its isomers, hydroxy sabina ketones, sabinic acid, sabina ketone, and pinic acid.

The estimated yield of sabina ketone in this work is in agreement with that, 50 ± 9%, measured by Hakola *et al.* (1994). Glasius *et al.* (1998) reported molar yields of sabinic acid and pinic acid in aerosol phase at 1.1% and 1.4%. Our yields for the two dicarboxylic acids in the aerosol phase are 0.4% and 0.3%. As we will discuss in Section 5, the absolute aerosol yield of a particular product depends on the temperature and the organic aerosol mass concentration in each system in which SOA is generated. Without the knowledge of the temperature and organic aerosol mass concentration in the system of Glasius *et al.*, it is difficult to make a meaningful comparison.

4.3. α-PINENE

Table XI shows yields of individual products in the gas and aerosol phases, as well as the total yields of both phases, in three α-pinene/O_3 experiments. Identified products in both the gas and aerosol phases account for 29–67% of the reacted α-pinene carbon mass. Products with a molar yield exceeding 1% include pinonaldehyde (6–19%), norpinonic acid and its isomers (4–13%), hydroxy pinonaldehydes (2–11%), pinonic acid (2–8%), pinic acid (3–6%), hydroxy pinonic acid (1–

Table XI. Gaseous and particulate product yields in the α-pinene/O_3 reaction

Product	Molar yield (%)									Aerosol yield (%) by mass		
	Gas			Aerosol			Total					
Experiment date	6/9/98a	6/9/98b	6/17/98a	6/9/98a	6/9/98b	6/17/98a	6/9/98a	6/9/98b	6/17/98a	6/9/98a	6/9/98b	6/17/98a
Pinic acid	1.2	2.1	2.7	1.8	3.9	2.8	3.0	6.0	5.5	2.5	5.3	3.9
Norpinic acid	0.04	0.03	0.04	0.08	0.09	0.05	0.1	0.1	0.09	0.1	0.1	0.06
Hydroxy pinonaldehydes	1.4	0.8	9.2	2.4	1.1	2.0	3.8	1.9	11.2	3.3	1.4	2.8
Pinonic acid	0.8	0.6	6.6	1.7	1.6	1.3	2.5	2.2	7.9	2.3	2.1	1.8
Norpinonic acid and isomer	2.2	5.4	9.8	2.1	4.8	2.8	4.3	10.2	12.6	2.6	5.9	3.4
Pinonaldehyde	9.6	5.7	18.1	0.8	0.3	0.9	10.4	6.0	19.0	1.0	0.4	1.1
Norpinonaldehyde	1.1	1.5	2.4	0.1	0.2	0.2	1.2	1.7	2.6	0.2	0.2	0.2
2,2-Dimethyl-cyclobutyl-1,3-dicarboxaldehyde	0.4	0.3	1.6	ND	ND	ND	0.4	0.3	1.6	0	0	0
Hydroxy pinonic acid	0.8	0.2	1.6	2.1	1.3	2.1	2.9	1.5	3.7	3.1	1.9	3.1
A_3[a]	1.5	0.6	3.8	ND	ND	ND	1.5	0.6	3.8	ND	ND	ND
A_{13}[a]	0.06	0.02	0.1	0.08	0.12	0.1	0.14	0.1	0.2	0.1	0.2	0.1
A_{14}[a]	0.03	trace	0.03	0.55	0.48	0.8	0.6	0.5	0.8	0.7	0.6	1.1
Total molar yield	19.1	17.2	56.0	11.7	13.9	13.0	30.8	31.0	69.1	15.9	18.1	17.6
Carbon-based total yield							29.9	29.1	66.8			
Aerosol yield measured by SEMS and CNC										17.6	18.6	15.9

[a] See Table VI for possible candidate structures.

4%), (2,2-dimethyl-3-acetyl)-cyclobutyl formate (1–4%), and norpinonaldehyde (1–3%).

In the 6/17/98a experiment, a much higher percentage of reacted α-pinene is accounted for by the identified products, as the four major products, pinonaldehyde, hydroxy pinonaldehydes, pinonic acid, and norpinonic acid and its isomers, are measured to have much higher yields than those in the experiments 6/9/98a and 6/9/98b. While measurement errors may account for part of the variation, the different reaction conditions also likely contribute to the variation. The 6/17/98a experiment is different from the experiments 6/9/98a and 6/9/98b in two aspects: (1) excessive α-pinene was used in the 6/17/98a experiment while excessive ozone was present in the prior two experiments, and (2) the denuder/filter sample was started 53 min after the initiation of the α-pinene/O_3 in the 6/19/98a experiment while in the other two experiments denuder/filter samples were collected more than 290 min after ozone oxidation of α-pinene started. One explanation is that the polar nature of the products makes them susceptible to be lost to the reactor wall by adsorption, as demonstrated for pinonaldehyde and caronaldehyde by Hallquist *et al.* (1997) in their experimental chamber. Actual product yields may be higher after accounting for wall loss, but wall loss does not account for all the yield variation. It is noted that for both the α-pinene/O_3 and the β-pinene/O_3 experiments, higher gas-phase yields were measured when excess monoterpene was present in the reaction systems. Presently we do not have a satisfactory explanation for this observation. Four previous studies have reported yields of some of the above products. The gas-phase yield of pinonaldehyde was measured to be 14.3 ± 2.4% (Alvarado *et al.*, 1998) and 19 ± 4% (Hakola *et al.*, 1994). In this work, the yield is estimated to be 5.7–18.1%, in general agreement with the values reported in the two previous studies. Hull (1981) reported total yields in both phases for four major products: Pinonic acid (27%), pinonaldehyde (15%), hydroxy pinonaldehyde (7%), and norpinonic acid (7%). We have measured or estimated the yields in both phases to be 2.1–7.9%, 6.5–19.0%, 1.8–11.2%, and 4.2–12.6%, respectively. The yield of pinonic acid measured by Hull is much higher than our yield. In Hull's study, no OH scavenger was added, and the mixing ratios of α-pinene used ranged from 110 to 509 ppmv, which is more than 1000 times higher than those in this work. It is difficult to make meaningful comparisons considering the very different reaction conditions investigated in the two studies. In the absence of OH scavengers, Hatakeyama *et al.* (1989) measured aldehyde yield in the gas-phase to be 51 ± 6% by FTIR absorption spectroscopy. In this study we have identified ten products with aldehyde functional group(s), i.e., pinonaldehyde, norpinonaldehyde, hydroxy pinonaldehydes (A_{12}), norpinonic acid and isomers (A_5), A_4, A_8, A_{11}, A_{12}, A_{13}, and A_{14}. The sum of yields for all these aldehyde products in the gas phase ranges from 14–45%. If one considers that the absence of OH scavenger would increase yields of aldehyde products such as pinonaldehyde, yield data from this study may be consistent with the result obtained by Hatakeyama *et al.* (1989).

Table XII. Gaseous and particulate product yields in the Δ^3-carene/O_3 reaction

Product	Molar yield (%)			Aerosol yield
	Gas	Aerosol	Total	by mass (%)
Pinic acid	0.83	0.33	1.2	0.46
3-Caric acid	0.64	1.3	1.9	1.8
Nor-3-caric acid	0.07	ND	0.07	ND
Hydroxy caronaldehydes	3.0	0.19	3.2	0.25
3-Caronic acid	2.7	1.5	4.2	2.1
Nor-3-caronic acid and isomers	1.8	0.54	2.3	0.68
Caronaldehyde	7.8	0.67	8.5	0.83
Norcaronaldehyde	Trace	Trace	Trace	Trace
Hydroxy 3-caronic acid	0.47	0.69	1.2	1.0
C_4[a]	0.31	0.39	0.70	0.54
C_5[a]	2.3	0.24	2.5	0.25
C_{10}[a]	0.22	ND	0.22	ND
Total molar yield	20.1	5.9	26.0	7.9
Carbon-based total yield			24.4	
Aerosol yield measured by SEMS and CNC				13.0

[a] See Table VII for possible candidate structures.

All the products added together account for 90–111% of the organic aerosol mass formed. The larger than 100% aerosol yield reflects the uncertainties associated with the estimated response factors for those products without available standards, and the assumption that SOA has a density of 1 g cm^{-3}. At 306–308 K, major aerosol components that make up more than 10% of the organic aerosol mass include pinic acid, hydroxy pinonaldehydes, pinonic acid, norpinonic acid and its isomers, and hydroxy pinonic acid.

Among all the monoterpenes, ozone oxidation of α-pinene is the most frequently studied reaction for its aerosol products. In previous studies, the molar yield of pinic acid and pinonic acid in the aerosol phase was measured to range from 0.2% to 1%, and 0.1–0.3%, respectively (Christoffersen *et al.*, 1998; Glasius *et al.*, 1998). The temperature and organic aerosol mass in their systems were not reported.

4.4. Δ^3-CARENE

Table XII shows the gas and aerosol phase yields of the individual products, as well as the total yields of both phases in one Δ^3-carene/O_3 experiment. Identified products in both the gas and aerosol phases account for 24% of the reacted Δ^3-carene carbon mass. Products with a molar yield exceeding 1% include caronaldehyde (8%), 3-caronic acid (4%), hydroxy caronaldehydes (3%), nor-3-caronic acid and isomers (2%), C_5 (2%), 3-caric acid (2%), hydroxy-3-caronic acid (1%), and pinic acid (1%). Caronaldehyde has been identified as a major product in a previous study with a yield of $\leq$8% in the gas phase (Hakola *et al.*, 1994). Here the gas-phase caronaldehyde yield is estimated to be 7.8%.

All the products added together account for 61% of the organic aerosol mass formed. Major aerosol products that contribute to $>$10% of organic aerosol mass are 3-caronic acid and 3-caric acid. Glasius *et al.* (1998) reported three aerosol products, 3-caric acid, 3-caronic acid, and nor-3-caric acid with aerosol phase yields of 0.5–5%, 0.1–0.7%, and 0.08–0.1%, respectively.

5. Gas-Particle Partitioning

Many products identified in this study are detected in both gas and aerosol phases. Gas-particle partitioning for semi-volatile organic compounds have been successfully described by the equilibrium relation:

$$K_{\mathrm{om},i} = \frac{F_i}{A_i \Delta M_o}\,, \tag{2}$$

where $K_{\mathrm{om},i}$ is the gas-particle partitioning coefficient of species i, A_i is the gas phase concentration (μg m^{-3}) of compound i, and F_i is the concentration of compound i (μg m^{-3}) in the aerosol phase (Odum *et al.*, 1996). A_i and F_i can be determined directly from denuder and filter samples, and ΔM_o is obtained from aerosol size distribution measurements. Table XIII lists the gas-particle partitioning coefficients of aerosol components generated in the ozone oxidation of the four monoterpenes.

Gas-particle partitioning coefficients of semi-volatile compounds depend on their vapor pressures (Pankow, 1987);

$$K_{\mathrm{om},i} = \frac{760RT}{MW_{\mathrm{om}} 10^6 \zeta_i p^o_{L,i}}\,, \tag{3}$$

where R is the ideal gas constant (8.206×10^{-5} m^3 atm mol^{-1} K^{-1}), T is temperature (K), MW_{om} is the number-averaged molecular weight of the organic matter (om) phase (g mol^{-1}), ζ_i is the molar fraction scale activity coefficient of compound i in the om phase, and $p^o_{L,i}$ is the sub-cooled liquid vapor pressure (mm Hg) of compound i. Sub-cooled liquid vapor pressures of the major products in the β-pinene/O_3 and α-pinene/O_3 systems have been estimated using a modification of the Clausius–Claperyron equation (Schwarzenbach *et al.*, 1993) (Table XIV). Measured $K_{\mathrm{om},i}$ values versus the estimated $p^o_{L,i}$ are shown in Figure 10. As Figure 10 illustrates, the lower the vapor pressure, the higher the corresponding $K_{\mathrm{om},i}$. For example, hydroxy pinonic acid, as a result of the presence of three polar functional groups, has the lowest vapor pressure ($\sim 10^{-5}$ mm Hg) among all identified products, and consequently exhibits the highest $K_{\mathrm{om},i}$ value. On the

Table XIII. Gas-particle partitioning coefficients ($m^3\ \mu g^{-1}$) of individual products at 306–308 K

α-Pinene/O_3		Δ^3-Carene/O_3		β-Pinene/O_3		Sabinene/O_3	
Compound	$K_{om,i}$	Compound	$K_{om,i}$	Compound	$K_{om,i}$	Compound	$K_{om,i}$
Pinic acid	0.028 ± 0.001	3-Caric acid	0.033	Pinic acid	0.035 ± 0.009	Sabinic acid	0.027
Hydroxy pinonaldehydes	0.019 ± 0.013	Hydroxy caronaldehydes	0.0010	Hydroxy pinaketones	0.0091 ± 0.0054	Hydroxy sabina ketones	0.0037
Pinonic acid	0.030 ± 0.005	3-Caronic acid	0.0090				
Norpinonic acid and its isomers	0.013 ± 0.005	Nor-3-caronic acid	0.0047	Norpinonic acid and its isomers	0.014 ± 0.001	Norsabinonic acid and its isomers	0.018
Pinonaldehyde	0.0012 ± 0.0003	Caronaldehyde	0.0014	3-Oxo-pine ketone	0.0010 ± 0.0005	3-Oxo-sabina ketone	0.0012
Hydroxy pinonic acid	0.040 ± 0.010	Hydroxy caronic acid	0.0231	Hydroxy pinonic acid	0.066 ± 0.026	Sabina ketone	0.00053
A_{13}	0.025 ± 0.003			Hydroxy norpinonic acid	0.016 ± 0.009		

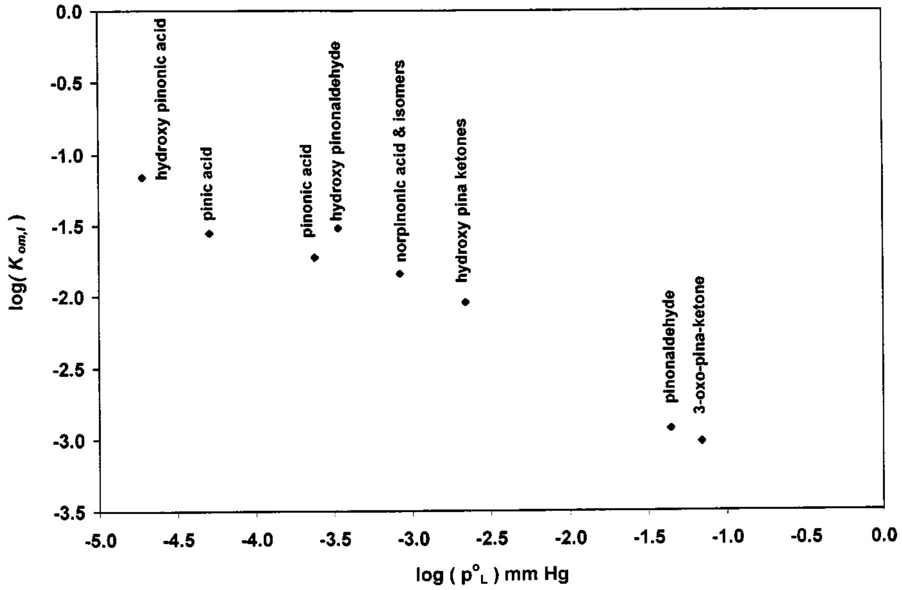


Figure 10. Measured $\log(K_{\mathrm{om},i})$ versus estimated log p_L^o for the major products in the β-pinene/O_3 and α-pinene/O_3 systems.

Table XIV. Sub-cooled liquid vapor pressure estimates

Compound	T_b (K)[a]	Vapor pressure estimates at 306 K[b]	
		mm Hg	ppmv
Hydroxy pinonic acid	606	1.9×10^{-5}	0.048
Pinic acid	601	5.1×10^{-5}	0.067
Hydroxy pinonaldehydes	577	2.4×10^{-4}	0.32
Pinonic acid	572	3.4×10^{-4}	0.45
Norpinonic acid and isomers	558	8.4×10^{-4}	1.1
Hydroxy pina ketone	542	2.2×10^{-3}	2.9
Pinonaldehyde	530	4.4×10^{-2}	58
3-Oxo-pina ketone	521	6.9×10^{-2}	91
Nopinone	482	4.7×10^{-1}	620

[a] T_b, boiling point at 1 atm if decomposition would not occur, estimated using Meissner's method (Rechsteiner, 1990). T_b is needed to estimate vapor pressure. Meissner's method underestimates the T_b for each of C_5–C_{10} n-alkanoic acids by ~6.5%, therefore a correction formula is obtained by a linear regression ($r^2 = 0.994$) for C_5–C_{10} n-alkanoic acids, and applied to the compounds of unknown T_b. This correction is also justified for carbonyl-containing compounds. For example, Meissner's method estimates that the T_b for nopinone is 453 K before correction, and 485 K after correction, which agrees well with the experimental value 482 K.

[b] Sub-cooled liquid vapor pressures are estimated using a modification of the Clausius-Claperyron equation (Schwarzenbach *et al.*, 1993).

other hand, the vapor pressure of pinonaldehyde and 3-oxo-pina ketone are higher than the –COOH bearing products, which correlates with the lowest $K_{\mathrm{om},i}$ values (Table XIII). Nopinone has an even higher vapor pressure than 3-oxo-pina ketone and is, as a result, expected to reside mainly in the gas-phase. Only trace amounts of nopinone were detected in any filter samples, confirming the influence of vapor pressure on the partitioning between the gas and aerosol phases. Similar trends are observed for SOA products in the ozone oxidation of the other two monoterpenes.

The aerosol phase fraction ϕ_i of a semi-volatile product is given by

$$\phi_i = \frac{F_i}{A_i + F_i} = \frac{\Delta M_o K_{\mathrm{om},i}}{1 + \Delta M_o K_{\mathrm{om},i}} . \tag{4}$$

As Equation (4) indicates, ϕ_i is controlled by the aerosol organic matter concentration ΔM_o available for absorption and the gas-aerosol partitioning coefficient $K_{\mathrm{om},i}$, which is a function of temperature and compound-dependent. Consequently, SOA chemical composition is a function of organic matter concentration and temperature. Figure 11 illustrates the dependence of ϕ_i on ΔM_o, using pinic acid as an example. The temperature dependence of SOA chemical composition was demonstrated by Jang and Kamens (1998), who observed that for SOA generated in the α-pinene/O_3 reaction, the more volatile SOA components reside in the particle phase to a much greater extent under cold conditions than warmer conditions. When reporting aerosol yield of an individual product and composition of SOA, it is necessary to include the organic aerosol mass concentration and associated temperature.

The yield of an individual product i in the aerosol phase (Y_i) can be expressed as

$$Y_i = \Delta M_o \frac{\alpha_i K_{\mathrm{om},i}}{1 + K_{\mathrm{om},i} \Delta M_o} , \tag{5}$$

where α_i is the individual mass-based stoichiometric coefficient of i. The overall SOA yield Y is then just the sum of the individual yields

$$Y = \sum_i Y_i = \Delta M_o \sum_i \left(\frac{\alpha_i K_{\mathrm{om},i}}{1 + K_{\mathrm{om},i} \Delta M_o} \right) . \tag{6}$$

Using Equation (6), a two-product model has successfully described the overall SOA yield Y as a function of stoichiometric coefficient α_i and partitioning coefficients $K_{\mathrm{om},i}$ of two hypothetical products, and ΔM_o, the total organic aerosol mass concentration (Odum *et al.*, 1996, 1997a, b; Hoffman *et al.*, 1997; Griffin *et al.*, 1999).

One of the major assumptions underlying the derivation of Equations (5) and (6) is that the total amount of a product is proportional to the amount of the parent hydrocarbon reacted. If this assumption holds, the SOA yield at any time $Y(t)$, should be described by Equation (6). Figure 12(a) shows the $Y(t)$ values as a function of organic aerosol mass for the 6/09/98a and 6/09/98b α-pinene/O_3 experiments.

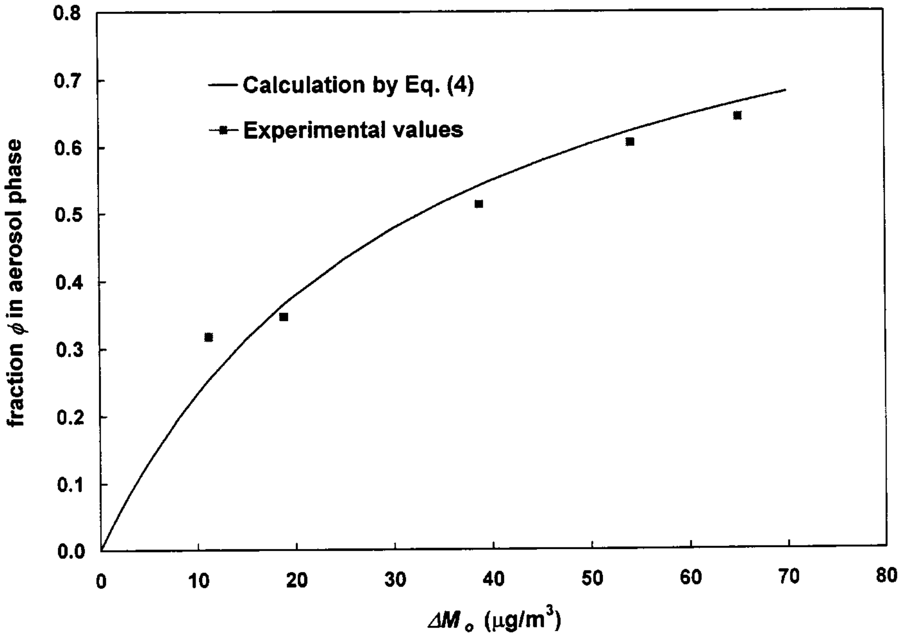


Figure 11. Fraction of pinic acid in aerosol phase as a function of organic aerosol mass concentration.

The experimentally determined time-dependent yield curves for both experiments can be closely represented by using Equation (6) and assuming two hypothetical products with $\alpha_1 = 0.262$, $K_{\mathrm{om},1} = 0.030$, $\alpha_2 = 0.062$, and $K_{\mathrm{om},2} = 0.0028$ (Figure 12(a)). On the other hand, a yield curve can also be constructed for each experiment by using Equation (6) and the experimentally determined α_i and $K_{\mathrm{om},i}$ values for the individual aerosol-phase products. The resulting curves fit well the experimental SOA yield curves (Figure 12(a)). Since the denuder/filter samples were taken at the end of the two experiments (Table I), the α_i and $K_{\mathrm{om},i}$ values obtained from these samples represent the SOA composition and product distribution between gas and aerosol phases at the end of the experiments. The fact that they also predict the SOA yields during earlier stages of the experiments indicates that in the α-pinene/O_3 system, the SOA composition and product distribution between gas and particle phase remains relatively unchanged over time. This is in agreement with the time profiles of α-pinene mixing ratio and organic aerosol mass concentration ΔM_o (Figure 12(b)). As Figure 12(b) shows, after most of the α-pinene is oxidized, the aerosol mass remains almost constant, which indicates that the SOA mass arises from either primary products or secondary products formed relatively rapidly.

Conversely, if the total amount of a product that is generated in the reaction is not proportional to the amount of the parent hydrocarbon reacted throughout an experiment, e.g., the relative chemical composition changes over the course of

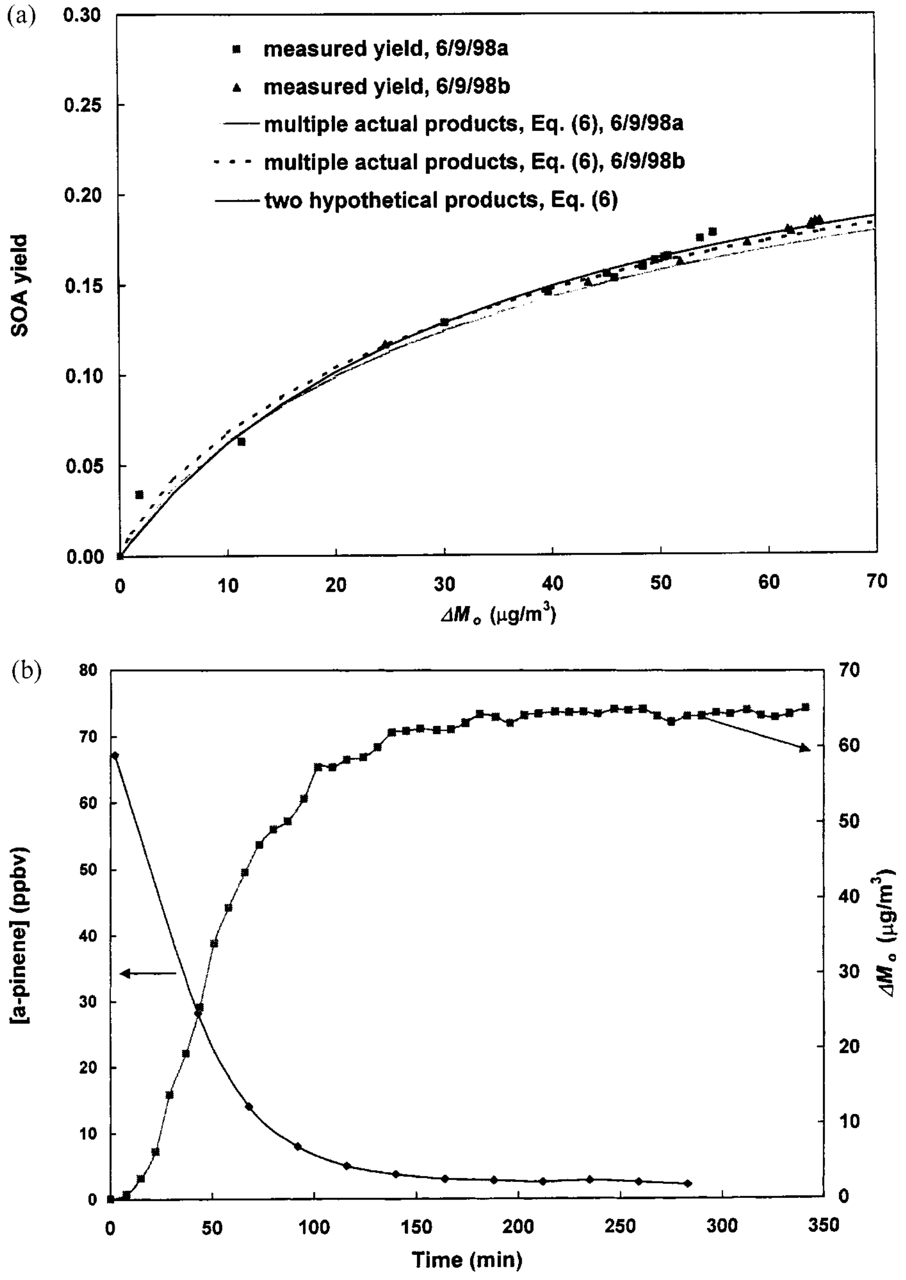


Figure 12. (a) Time-dependent secondary organic aerosol yields as a function of organic aerosol mass for two α-pinene/O_3 experiments. (b) α-Pinene mixing ratio and organic aerosol mass concentration as a function of time.

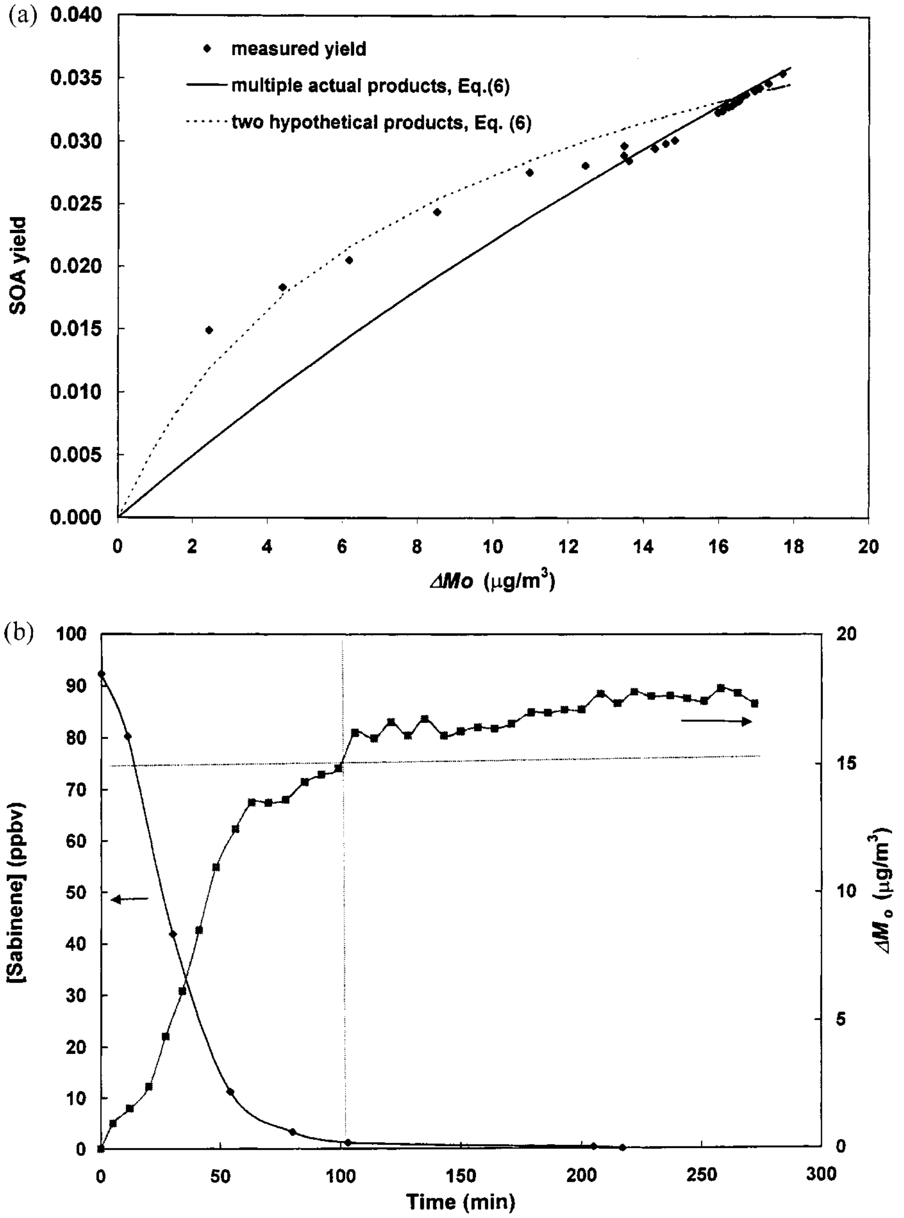


Figure 13. (a) Time-dependent secondary organic aerosol yields as a function of organic aerosol mass for the sabinene/O_3 reaction. (b) Sabinene mixing ratio and organic aerosol mass concentration as a function of time.

the experiment, one set of α_i and $K_{\mathrm{om},i}$ values will not describe the SOA yields over the reaction time. The time-dependent SOA yield in the sabinene/O_3 reaction appears to be such an example (Figure 13(a)). As shown in Figure 13(a), a two-product model, using Equation (6) and assuming two hypothetical products with $\alpha_1 = 0.041$, $K_{\mathrm{om},1} = 0.154$, $\alpha_2 = 0.51$, and $K_{\mathrm{om},2} = 0.0005$, describes the time-dependent aerosol yield reasonably well up to $\Delta M_o \sim 15\ \mu\mathrm{g/m}^3$, which corresponds to a reaction time of ~100 min and 99% sabinene consumption. The $Y(t)$ curve computed using Equation (6) and the α_i, and $K_{\mathrm{om},i}$ values for multiple actual products fits well the measured aerosol yields at the later stage, but represents poorly the early-stage yields. The denuder/aerosol sample was taken 232 minutes after the reaction started, therefore the measured α_i, and $K_{\mathrm{om},i}$ values of individual products reflect the SOA composition in the later stage of the experiment. The above analysis suggests that slowly forming secondary or tertiary products play a role in the aerosol formation in the sabinene/O_3 reaction. The contribution of secondary products is further evidenced by the time profiles of sabinene mixing ratio and organic aerosol mass concentration ΔM_o. As shown in Figure 13(b), at ~100 min, while nearly all the sabinene is reacted, the organic aerosol mass continues to grow.

For reaction systems such as α-pinene/O_3 reaction, one set of α_i and $K_{\mathrm{om},i}$ values is sufficient to describe the kinetics of aerosol formation. On the other hand, for reaction systems such as the sabinene/O_3 reaction, more than one set of α_i and $K_{\mathrm{om},i}$ values are necessary to describe the evolution of aerosol mass.

6. Mechanisms of Product Formation

Based on known reaction mechanisms for alkene-O_3 reactions, it is possible to propose reaction schemes to account for most of the observed products.

6.1. β-PINENE/O_3 REACTION

Figure 14 shows reaction sequences leading to the products in the β-pinene/O_3 reaction. The reaction of β-pinene with O_3 proceeds by initial O_3 addition to the C=C bond to yield an energy-rich ozonide, which rapidly decomposes to form nopinone and a C_9 biradical. Many of the observed products are formed from the subsequent reactions of the C_9 biradical. The energy-rich C_9 biradical undergoes isomerization to give rise to two enehydroperoxides (EN_1 and EN_2) with excess energies. This is the so-called hydroperoxide channel. The formation of hydroxy pina ketones (P_4) are a result of stabilization of EN_1 and EN_2 through collision (Niki *et al.*, 1987; Martinez and Herron, 1987, 1988; Atkinson, 1997). One additional pathway for EN_2 is to produce 3-oxo-pina ketone (P_{11}) by loss of a H_2 molecule. This pathway is not operative for EN_1, because the OH group is attached to a tertiary C, and no H-atom is available for loss of a H_2 molecule. It is postulated that the energized 3-hydroxy pina ketone could undergo unimolecular dissociation

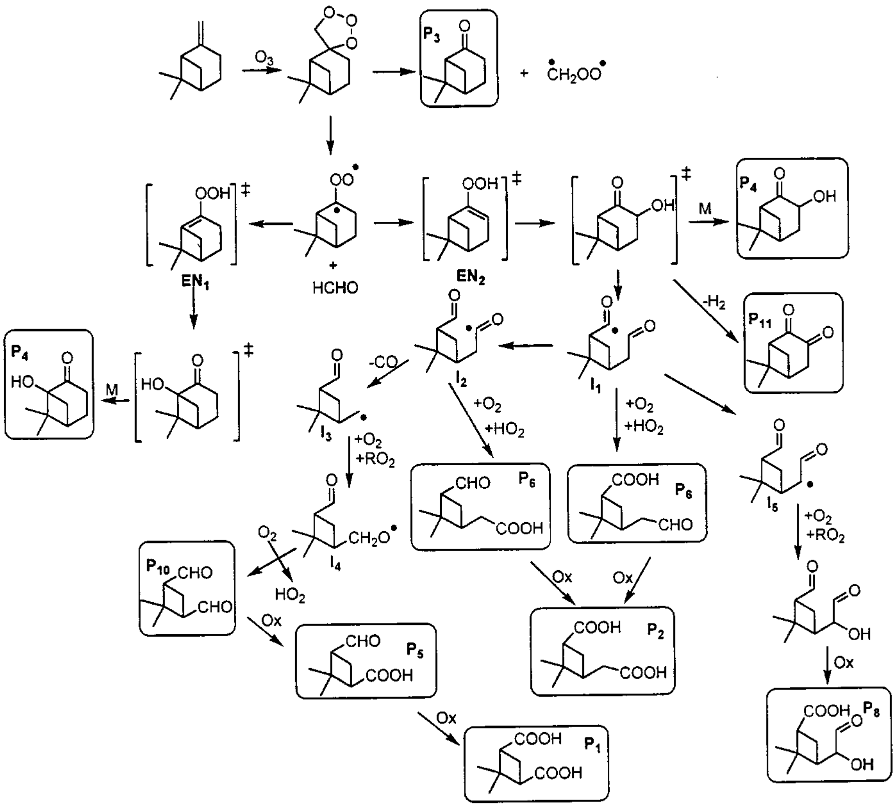
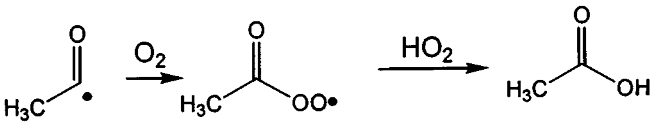


Figure 14. Reaction mechanism of O_3/β-pinene reaction.

to form an acetyl-like radical I_1 and I_2. For the acetyl radical, it has been established that its subsequent reactions with O_2 and HO_2 radical lead to the formation of acetic acid (Niki *et al.*, 1985; Moortgat *et al.*, 1989).



Similarly, the reaction of I_1 and I_2 with O_2, and subsequently with HO_2 would lead to P_6. I_2 can also lose a molecule of CO to form I_3, which reacts with O_2, and a peroxy radical RO_2 to form I_4. It follows that I_4 loses one H-atom to an O_2 molecule to produce P_{10}. The formation of P_5, norpinic acid (P_1), and pinic acid (P_2) is presupposed to result from oxidation of their corresponding aldehydes, P_{10}, P_5 and P_6, respectively, although the explicit oxidation mechanism is unclear.

The formation pathway for a possible candidate of P_8 is proposed to arise from I_5, which can be formed from isomerization of I_1. It is difficult to construct plausible formation pathways for pinonic acid and hydroxy pinonic acid.

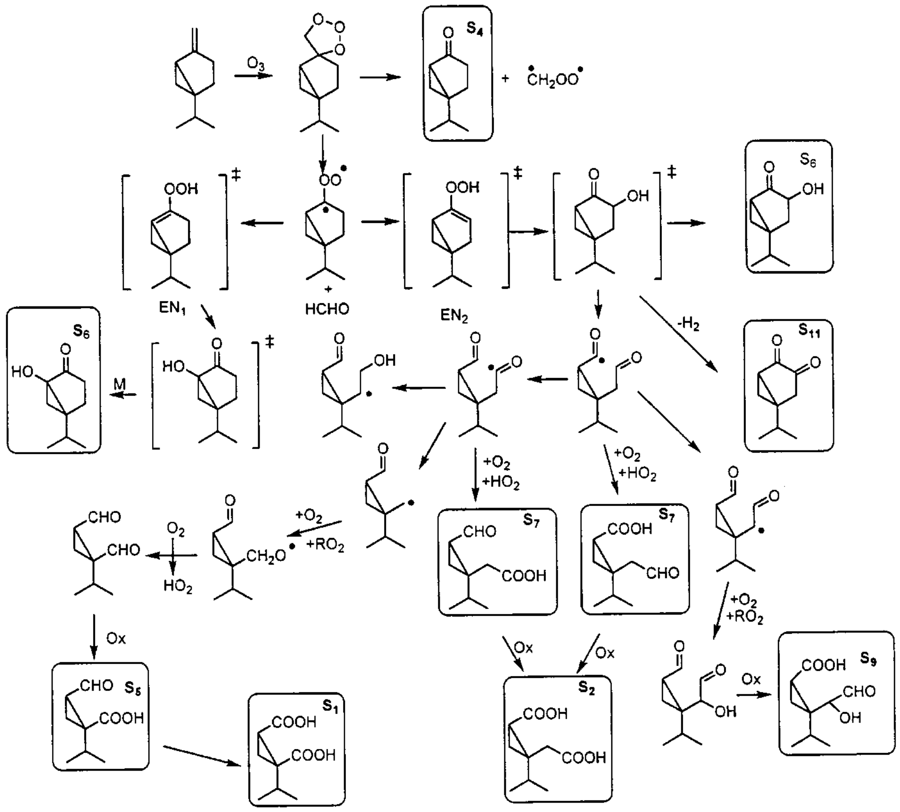


Figure 15. Reaction mechanism of O_3/sabinene reaction.

6.2. SABINENE/O_3 REACTION

Figure 15 depicts reaction pathways that account for most of the products observed from the sabinene/O_3 reaction. The many pairs of analogous products in the sabinene/O_3 and β-pinene/O_3 reactions are easily explained by the same reaction pathways derived from O_3 attack of the external C=C bond.

The observation of pinic acid in the sabinene/O_3 reaction is difficult to explain in terms of plausible gas-phase reaction mechanisms. It is not clear whether aerosol surface plays a role in the formation of pinic acid via heterogeneous reactions. There is evidence that isomerization of monoterpenes can take place on acidic surfaces (Pio and Valente, 1998). In addition, Coeur *et al.* (1997) observed that ~70% of sabinene isomerizes to other monoterpenes of lower ring tension when it is sampled onto Tenax TA or Carboxen sorbents. Sabinic acid may undergo similar isomerization to pinic acid on particle surfaces.

As the chemical structures of the two unique products, S_8 and S_{12}, in the sabinene/O_3 reaction remain uncertain, we do not attempt to propose formation mechanisms for them.

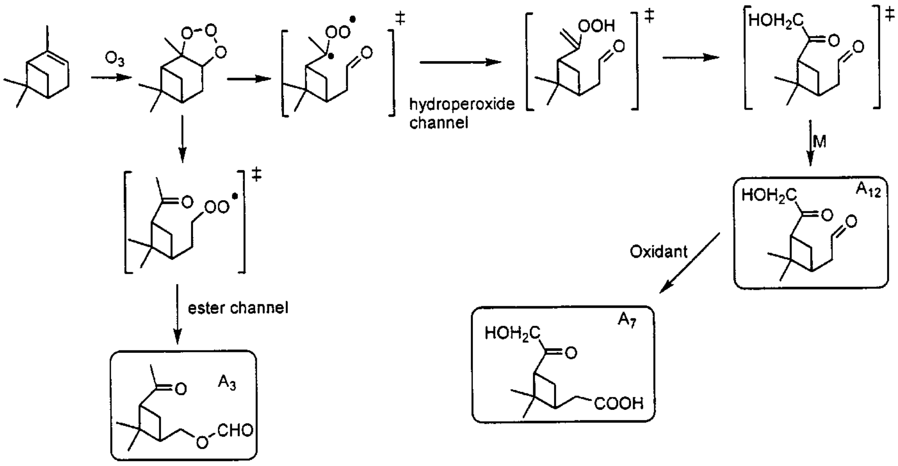


Figure 16. Formation mechanism for A_3 and A_7 in the O_3/α-pinene reaction.

6.3. α-PINENE/O_3 AND Δ^3-CARENE/O_3

The formation mechanisms of products from ozone oxidation of α-pinene have been described in an earlier paper (Yu *et al.*, 1998). Here we only discuss the formation pathways for the newly identified products (Figure 16). The formation of A_3 arises from isomerization of the Criegee biradical, known as the ester channel (Atkinson, 1997). Hydroxy pinonic acid is postulated to result from its aldehyde precursor, 10-hydroxy-pinonaldehyde (A_{12}). We do not yet attempt to propose formation mechanism for A_{11}, A_{13} and A_{14}, as their chemical structures are not yet certain.

The formation pathways for most of the products in the Δ^3-carene/O_3 reaction (Figure 17) are similar to those in the α-pinene/O_3 reaction, as a result of the internal C=C bond common to both reactants. Those products unique to the Δ^3-carene/O_3 reaction do not have obvious routes of formation. The presence of pinic acid in the Δ^3-carene/O_3 reaction system may derive from similar routes to those responsible for the formation of pinic acid in the sabinene/O_3 reaction system.

7. Summary and Conclusions

This study has identified a substantial fraction of the particulate products from ozone oxidation of each of the four monoterpenes: α-pinene, β-pinene, Δ^3-carene, and sabinene. β-Pinene and sabinene are structurally analogous in that both are bicyclic and have an external unsaturated bond where ozone oxidation takes place. α-Pinene and Δ^3-carene also share one common structural moiety, an internal unsaturated bond. A number of analogous product pairs, including major products, have been identified for each pair of monoterpenes. These products are consistent with the established understanding of the mechanism of ozone-alkene reactions.

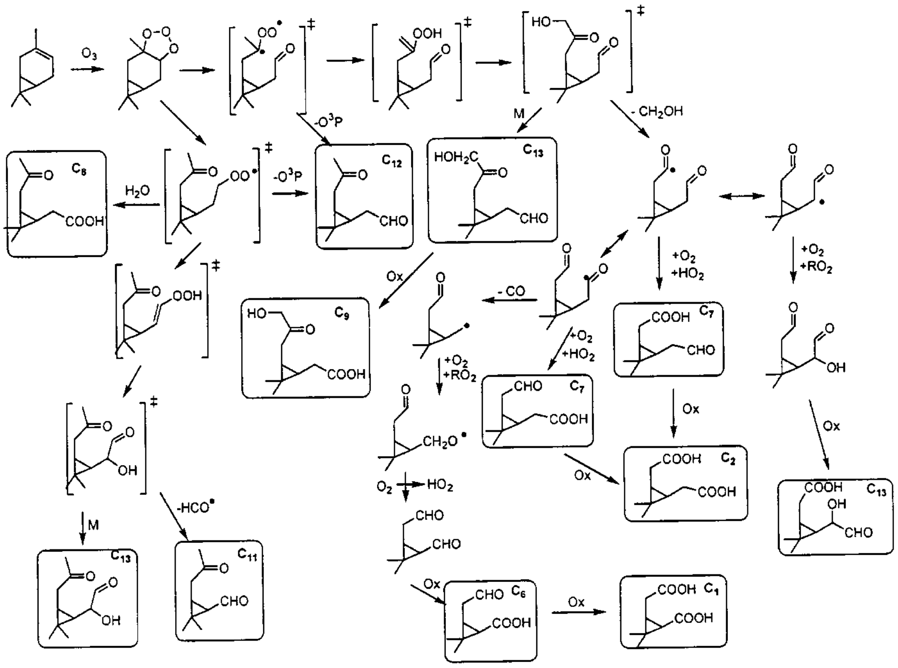


Figure 17. Reaction mechanism of O_3/Δ^3-carene reaction.

In addition to expected products, a number of products having minor yields that are unique to each monoterpene have also been detected. One interesting finding that is yet to be explained is the presence of pinic acid in both the sabinene/O_3 and Δ^3-carene/O_3 reactions.

Yields of individual products in both the gas and aerosol phases have been determined or estimated, thus providing a direct measure of the gas-particle partitioning of each product. The identified products account for a significant fraction of the secondary organic aerosol for each of the parent hydrocarbons. Identified products, in both gas and aerosol phases, are estimated to account for about 34–50%, 57%, 29–67%, and 24% of the total reacted carbon mass for β-pinene, sabinene, α-pinene, and Δ^3-carene, respectively. Whereas these percentages exceed those of previous studies, a significant fraction of the monoterpenes reacted still remains unaccounted for. As the yields of many products are estimated using the response factor of surrogates, an improved mass balance awaits authentic standards or new analytical techniques that do not require authentic standards. Based on experimentally measured gas-particle partitioning coefficients of individual oxidation products, it is possible to evaluate the extent to which overall aerosol yields observed in smog chamber experiments can be represented by the stoichiometric yields and gas-particle partitioning of the individual products.

Based on the nature and yield of various aerosol components, products such as pinic acid, pinonic acid, norpinonic acid, hydroxy pinonic acid, and hydroxy pinonaldehydes can act as molecular markers for secondary organic aerosol derived from biogenic sources.

Acknowledgements

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References

Alvarado, A., Tuazon, E. C., Aschmann, S. M., Atkinson, R., and Arey, J., 1998: Products of the gas-phase reactions of O(^{3}P) atoms and O_3 with α-pinene and 1,2-dimethyl-1-cyclohexene, *J. Geophys. Res.* **103**, 25541–25551.

Arey, J., Atkinson, R., and Aschmann, S. M., 1990: Product study of the gas-phase reactions of monoterpenes with the OH radical in the presence of NO_x, *J. Geophys. Res.* **95**, 18539–18546.

Atkinson, R., 1997: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, *J. Phys. Chem. Ref. Data* **26**, 215.

Atkinson, R. and Carter, W. P. L., 1984: Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions, *Chem. Rev.* **84**, 437–470.

Calogirou, A., Larsen, B. R., and Kotzias, D., 1999: Gas phase terpene oxidation products: A review, *Atmos. Environ.*, **33**, 1423–1439.

Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S., 1988: The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, *Science* **241**, 1473–1475.

Chew, A. A. and Atkinson, R., 1996: OH radical formation yields from the gas-phase reaction of O_3 with alkenes and monoterpenes, *J. Geophys. Res.* **101**, 28649–28653.

Christoffersen, T. S., Hjorth, J., Horie, O., Jensen, N. R., Kotzias, D., Molander, L. L., Neeb, P., Ruppert, L., Winterhalter, R., Virkkula, A., Wirtz, K., and Larsen, B. R., 1998: Cis-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of α-pinene, *Atmos. Environ.* **32**, 1657–1961.

Coeur, C., Jacob, V., Denis, I., and Foster, P., 1997: Decomposition of α-pinene and sabinene on solid sorbents, Tenax TA and Carboxen, *J. Chromatogr.* **786**, 185–187.

Glasius, M., Duane, M., and Larsen, B. R., 1999: Analysis of polar terpene oxidation products in aerosols by liquid chromatography ion trap mass spectrometry (MS^n), *J. Chromatogr.*, in press.

Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R, Hjorth J., Duane, M., Kotzias, D., and Larsen, B. R., Carboxylic acids in secondary aerosols from O_3 and OH oxidation of cyclic monoterpenes, In *Proceedings of the fifth EUROTRAC Symposium*, Garmish-Partenkirchen, March 23–27, 1998.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H., 1999: Organic aerosol formation from the oxidation of biogenic hydrocarbon, *J. Geophys. Res.*, **104**, 3555–3568.

Grosjean, D., 1985: Wall loss of gaseous pollutants in outdoor Teflon chamber, *Environ. Sci. Technol.* **19**, 1059–1065.

Grosjean, D., William II, E. L., Grosjean E., Andino, J. M., and Seinfeld, J. H., 1993: Atmospheric oxidation of biogenic hydrocarbons: reaction of ozone with β-pinene, D-limonene and *trans*-caryophyllene, *Environ. Sci. Technol.* **27**, 2754–2758.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., and Lerdau, M., 1995: A global model of natural volatile organic compound emissions, *J. Geophys. Res.* **100**, 8873–8892.

Gundel, L. A., Lee, V. C., Mahanama, K. R. R., Stevens, R. K., and Daisey, J. M., 1995: Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders, *Atmos. Environ.* **29**, 1719–1733.

Hakola, H., Arey, J., Aschmann, S. M., and Atkinson, R., 1994: Product formation from the gas-phase reactions of OH radicals and O_3 with a series of monoterpenes, *J. Atmos. Chem.* **18**, 75–102.

Hallquist, M., Wangberg, I., and Ljungstrom, E., 1997: Atmospheric fate of carbonyl oxidation products originating from α-pinene and $\triangle^3$-carene: Determination of rate of reaction with OH and NO_3 radicals, UV absorption cross sections, and vapor pressure, *Environ. Sci. Technol.* **31**, 3166–3172.

Hart, K. M. and Pankow, J. F., 1994: High-volume air sampler for particle and gas sampling. 2. Use of backup filters to correct for the adsorption of gas-phase polycyclic aromatic hydrocarbons to the front filter, *Atmos. Environ.* **28**, 655–661.

Hatakeyama, S., Izumi, K., Fukuyama, T, and Akimoto, H., 1989: Reactions of ozone with α-pinene and β-pinene in air: Yields of gaseous and particulate products, *J. Geophys. Res.* **94**, 13013–13024.

Hoffmann, T., Bandur, R., Marggraf, U., and Linscheid, M., 1998: Molecular composition of organic aerosols formed in the α-pinene/O_3 reaction: Implication for new particle formation processes, *J. Geophys. Res.* **103**, 25569–25578.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D, Flagan, R. C., and Seinfeld, J. H., 1997: Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *J. Atmos. Chem.* **26**, 189–222.

Hull, L. A., 1981: Terpene ozonolysis products, in J. J. Bufalini and R. R. Arnts (eds), *Atmospheric Biogenic Hydrocarbons Vol. 2, Ambient Concentrations and Atmospheric Chemistry*, Ann Arbor Science, Ann Arbor, pp. 161–185.

Jang, M. and Kamens, R. M., 1998: Newly characterized products and composition of secondary aerosols from the reaction of α-pinene with ozone, *Atmos. Environ.* **33**, 459–474.

Kamens, R. M., Jeffries, H. E., Gery, M. W., Wiener, R. W., Sexton, K. G., and Howe, G. B., 1981: The impact of α-pinene on urban smog formation: an outdoor smog chamber study, *Atmos. Environ.* **15**, 969–981.

Larsen, B. R., Lahaniati, M., Calogirou, A., and Kotzias, D., 1998: Atmospheric oxidation products of terpenes: a new nomenclature, *Chemosphere* **37**, 1207–1220.

Le Lacheur, R. M., Sonnenberg, L. B., Singer, P. C., Christman, R. F., and Charles, M. J., 1993: Identification of carbonyl compounds in environmental samples, *Environ. Sci. Technol.* **27**, 2745–2753.

Martinez, R. I. and Herron, J. T., 1987: Stopped-flow studies of the mechanisms of ozone-alkene reactions in the gas-phase: Tetramethylethylene, *J. Phys. Chem.* **91**, 946–953.

Martinez, R. I. and Herron, J. T., 1988: Stopped-flow studies of the mechanisms of ozone-alkene reactions in the gas phase: *trans*-2-butene, *J. Phys. Chem.* **92**, 4644–4648.

McDow, S. R. and Huntzicker, J. J., 1990: Vapor adsorption artifact in the sampling of organic aerosol: Face velocity effects, *Atmos. Environ.* **24A**, 2563–2571.

Moortgat, G. K., Veyret, B., and Lesclaux, R., 1989: Kinetics of the reaction of HO_2 with $CH_3C(O)O_2$ in the temperature range 253-368K, *Chem. Phys. Lett.* **160**, 443–447.

Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., 1985: FTIR study of the kinetics and mechanism for Cl-atom-initiated reactions of acetaldehyde, *J. Phys. Chem.* **89**, 588–591.

Niki, H., Maker, P. D., Savage, C. M., Breitenbach, L. P., and Hurley, M. D., 1987: FTIR spectroscopic study of the mechanism for the gas-phase reaction between ozone and tetramethylethylene, *J. Phys. Chem.* **91**, 941–946.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H., 1996: Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.* **30**, 2580–2585.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H., 1997a: The atmospheric aerosol-forming potential of whole gasoline vapor, *Science* **276**, 96–99.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H., 1997b: Aromatics, reformulated gasoline, and atmospheric organic aerosol formation, *Environ. Sci. Technol.* **31**, 1890–1897.

Palen, E. J., Allen, D. T., Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C., 1992: Fourier transformation infrared analysis of aerosol formed in the photooxidation of isoprene and β-pinene, *Atmos. Environ. Part A* **26**, 1239–1251.

Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C., 1991: Aerosol formation in the photooxidation of isoprene and β-pinene, *Atmos. Environ.* **25A**, 997–1008.

Pankow, J. F., 1987: Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, *Atmos. Environ.* **21**, 2275–2283.

Pio, C. A. and Valente, A. A., 1998: Atmospheric fluxes and concentrations of monoterpenes in resin-trapped pine forest, *Atmos. Environ.* **32**, 683–691.

Rechsteiner Jr., C. E., 1990: Boiling Point, in Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. (eds), *Handbook of Chemical Property Estimation Methods*, American Chemical Society, Washington D.C.

Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M., 1993: *Environmental Organic Chemistry*, John Wiley & Sons, New York, pp. 70–75.

Yu, J., Flagan, R. C., and Seinfeld. J. H., 1998: Identification of Products Containing —COOH, —OH, and —C=O in Atmospheric Oxidation of Hydrocarbons, *Environ. Sci. Technol.* **32**, 2357–2370.

Yu, J., Jeffries, H. E., and Le Lacheur, R. M., 1995: Identifying airborne carbonyl compounds in isoprene atmospheric photooxidation products by their PFBHA oximes using gas chromatography/Ion trap mass spectrometry, *Environ. Sci. Technol.* **29**, 1923–1932.

Wang, S-C., Paulson, S. E., Grosjean, D., Flagan, R. C., and Seinfeld, J. H., 1992: Aerosol formation and growth in atmospheric organic/NO$_x$ systems- I. Outdoor smog chamber studies of C7- and C8-hydrocarbons, *Atmos. Environ.* **26A**, 403–420.

Zhang, S-H., Shaw, M., Seinfeld, J. H., and Flagan, R. C., 1992: Photochemical aerosol formation from α-pinene and β-pinene, *J. Geophys. Res.* **97**, 20717–20729.