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Identification of Products Containing −COOH, −OH, and −C═O in Atmospheric Oxidation of Hydrocarbons

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Atmospheric oxidation of hydrocarbons by hydroxyl radicals and ozone leads to products containing −COOH, −OH, and −C═O functional groups. The high polarity of such compounds precludes direct GC−MS analysis. In addition, many such compounds often exist in a single sample at trace levels. An analytical method has been developed to identify compounds containing one or more functional groups of carbonyl, carboxy, and hydroxy in atmospheric samples. In the 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). The derivatives are easily resolved by a GC column. The chemical ionization mass spectra of these derivatives exhibit several pseudomolecular ions, allowing unambiguous determination of molecular weights. Functional group identification is accomplished by monitoring the ions in the electron ionization mass spectra that are characteristic of each functional group derivative: *m/z* 181 for carbonyl and *m/z* 73 and 75 for carboxyl and hydroxy groups. The method is used to identify products in laboratory studies of ozone oxidation of α-pinene and Δ^3-carene. Among products from ozone oxidation of α-pinene, we have detected pinonaldehyde, norpinonaldehyde, pinonic acid, norpinonic acid, C_{10} hydroxy dicarbonyls, pinic acid, 2,2-dimethyl-3-(formylmethyl)-cyclobutane-formic acid, and a product that has a molecular weight of 156 and contains a C═O and a COOH/OH group. The latter two products have not been reported previously. Δ^3-Carene is structurally analogous to α-pinene in that both have an internal unsaturated bond where ozone oxidation takes place. We have also identified the corresponding analogous products, of which all but caronaldehyde are reported for the first time.

Introduction

Atmospheric oxidation of hydrocarbons by species such as the hydroxyl radical and ozone frequently leads to products containing −C═O (carbonyl), −COOH (carboxy), and −OH (hydroxy) functional groups. Oxidation of alkanes with a carbon chain length of $\geq C_4$, mainly initiated by OH radical attack, forms hydroxy carbonyl products through isomerization of alkoxy radical intermediates at increasing yields with increasing carbon numbers. For $\geq C_5$ *n*-alkanes, hydroxy carbonyls are dominant products (*1*−*4*). Oxidation of hydrocarbons containing C═C bonds can be initiated by both O_3 and OH radicals. Studies of simple alkenes have established that subsequent reactions lead to the formation of carbonyls, hydroxy carbonyls, dicarbonyls, carboxylic acids, and oxocarboxylic acids (*2, 5*−*11*).

Higher molecular weight compounds containing −OH, −COOH, and −C═O groups are expected to be important components of secondary organic aerosols (*12*). Experimental evidence suggests that compounds with these moieties are significant fractions of aerosol organics. Allen and co-workers (*13*−*15*) analyzed aerosols formed in photooxidation of β-pinene, 1-octene, and 1,3,5-trimethylbenzene, using FTIR coupled with a low-pressure impactor, and found that functional groups such as −C═O, −OH, −COOH, and nitrate dominate the products. Aerosol formed from cyclohexene and methylcyclohexene photooxidation also revealed dicarboxylic acids and other α,ω-difunctional oxygenates bearing carboxyl, formyl, hydroxyl, and nitrate groups as major products (*16*−*18*).

Information on these oxidation products of hydrocarbons is important to elucidate the atmospheric hydrocarbon reaction mechanism and to understand the formation mechanism of secondary organic aerosols. However, detecting and identifying compounds with these polar functionalities remain a demanding task. Such compounds are expected to exist at trace levels. Their polarity hinders identification and quantification by conventional analytical techniques, as the compounds are easily lost to the surfaces of injectors and columns. We report here a two-step derivatization technique, coupled with electron and chemical ionization mass spectrometry, to identify and detect compounds with −C═O, −OH, and −COOH moieties. In this method, −C═O groups react with O-(2,3,4,5,6-pentafluorobenzyl)hydroxy amine (PFBHA) to form oxime derivatives, then −COOH and −OH groups react with a silylation reagent N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) to form trimethylsilyl (TMS) derivatives (Figure 1). The first derivatization step prevents conversion of carbonyls to enols, which could react with BSTFA and complicate data interpretation.

Multistep derivatization techniques have long been used to detect and identify compounds containing multiple functional groups of carbonyl, carboxy, and hydroxy (*19*−*27*). Le Lacheur et al. (*24*) suggested a three-step derivatization technique: PFBHA derivatization of carbonyl groups, methylation of carboxy groups, and silylation of hydroxy groups. Also, a two-step derivatization technique that combines PFBHA derivatization and methylation has been used to detect oxoacids in biological and aqueous environmental samples (*20, 21, 26, 27*). Third, a PFBHA/silylation two-step derivatization technique has been applied to determine ketosteroids, oxoacids, and hydroxy aldehydes in biological samples (*19, 22, 23, 25*). The substitution of methylation with silylation enables simultaneous derivatization of carboxy and hydroxy functional groups. Here, we have modified the PFBHA/silylation technique for atmospheric samples collected under simulated atmospheric conditions, and explored electron ionization (EI) and chemical ionization (CI) mass spectrometry as a tool for identifying

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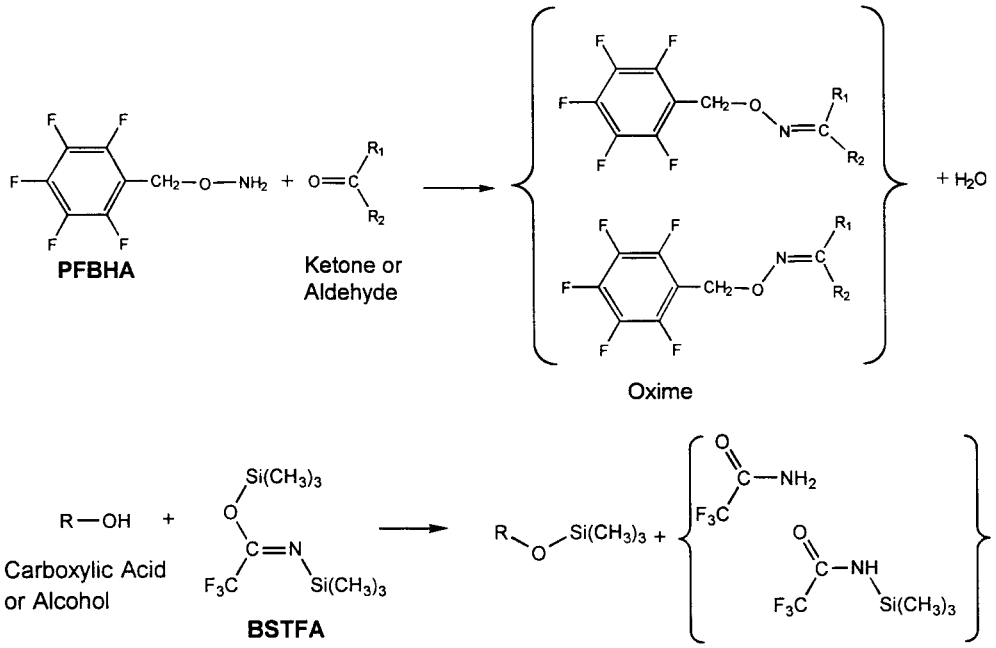


FIGURE 1. Derivatization reactions. (Top) PFBHA derivatizes a carbonyl group. (Bottom) BSTFA derivatizes an −OH group in acids and alcohols.

TABLE 1. Model Compounds

compd	molecular formula	MW[a]	derivative MW
	Group I: Mono- and Dicarboxylic Acids		
hexanoic acid	$CH_3(CH_2)_4COOH$	116	188
heptanoic acid	$CH_3(CH_2)_5COOH$	130	202
octanoic acid	$CH_3(CH_2)_6COOH$	144	216
nonanoic acid	$CH_3(CH_2)_7COOH$	158	230
benzoic acid	C_6H_5COOH	122	194
p-toluic acid	$p\text{-}CH_3C_6H_4COOH$	136	208
oxalic acid	HOOCCOOH	90	234
malonic acid	$HOOCCH_2COOH$	104	248
maleic acid	$HOOCCH_2{=}CH_2COOH$	116	260
succinic acid	$HOOC(CH_2)_2COOH$	118	262
glutaric acid	$HOOC(CH_2)_3COOH$	132	276
adipic acid	$HOOC(CH_2)_4COOH$	146	290
	Group II: Hydroxy Carboxylic Acids		
glycolic acid	$HOCH_2COOH$	76	220
lactic acid	$CH_3CH_2(OH)COOH$	80	234
	Group III: Carboxylic Acids with Carbonyl group		
glyoxylic acid	HC(O)COOH	74	341
pyruvic acid	$CH_3C(O)COOH$	88	355
ketomalonic acid	HOOCC(O)COOH	118	457
succinic semialdehyde	$HC(O)(CH_2)_2COOH$	102	369
oxalacetic acid	$HOOCCH_2C(O)COOH$	132	471
2-ketoglutaric acid	$HOOCC(O)(CH_2)_2COOH$	146	485
3-oxoglutaric acid	$HOOCCH_2C(O)CH_2COOH$	146	485
cis-pinonic acid	$CH_3C(O)C_4H_4(CH_3)_2CH_2COOH$	184	451
	Group IV: Hydroxy Aldehydes and Ketones		
glycolaldehyde	$HOCH_2CHO$	60	327
hydroxyacetone	$HOCH_2C(O)CH_3$	74	341
glyceraldehyde	$HOCH_2CH(OH)CHO$	90	429
3-hydroxy-benzaldehyde	$HO(C_6H_4)CHO$	122	389

[a] Molecular weight.

unknown compounds. To our knowledge, the application of the PFBHA/BSTFA double derivatization technique, coupled with EI and CI mass spectrometry for identifying unknown compounds, has not been reported for air samples.

Model compounds are examined first for their EI and CI mass spectra fragment patterns. Examples are then given to demonstrate how this method is used to identify products from atmospheric oxidation of two biogenic hydrocarbons, α-pinene and Δ^3-carene.

Experimental Section

Materials. All standards and PFBHA were purchased from Aldrich (Milwaukee, WI) and used without purification. BSTFA was from Pierce (Rockford, IL) and contains 1%

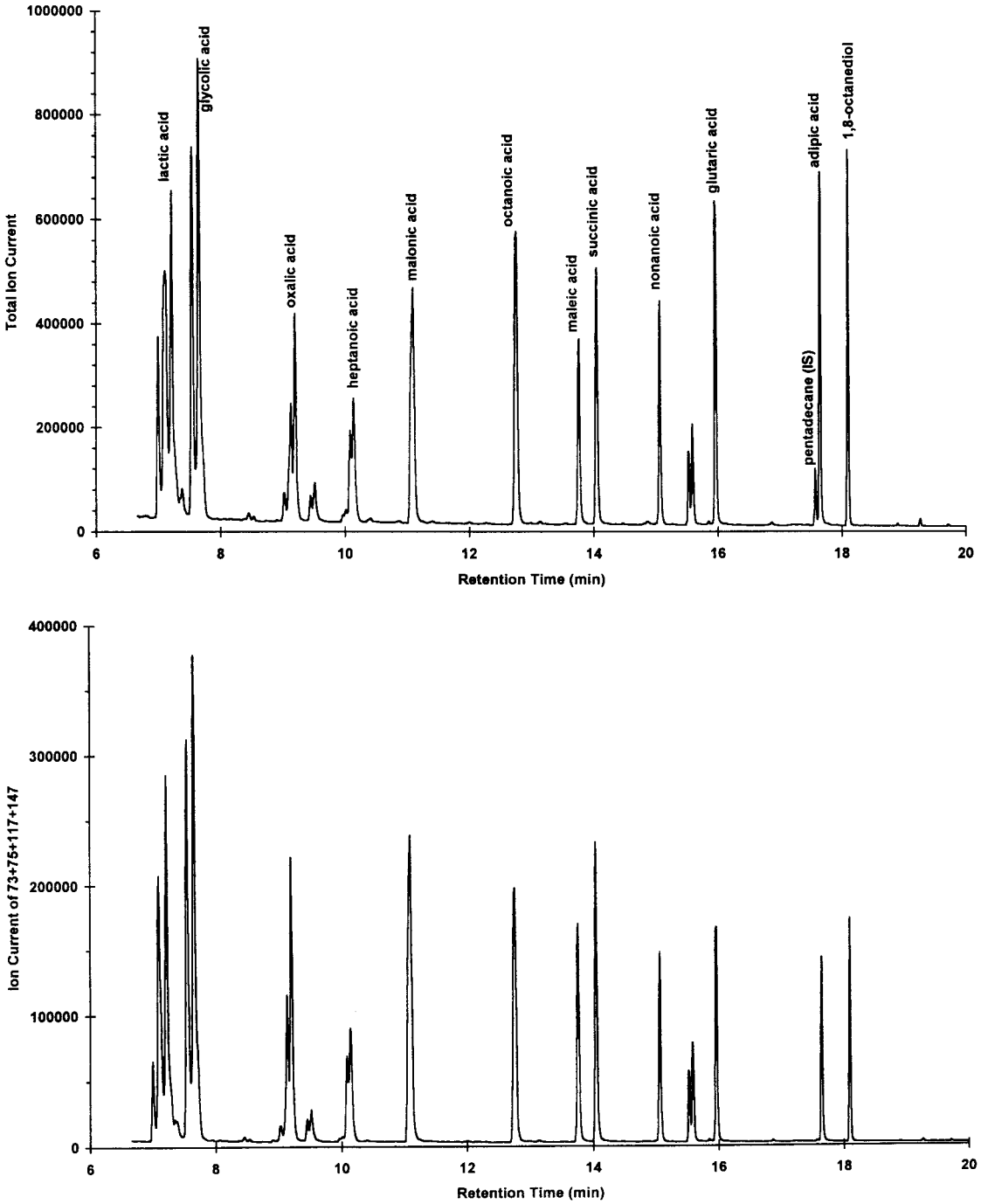


FIGURE 2. Chromatogram of a derivatized mixture of model compounds bearing −OH and −COOH groups. (Top) Total ion current. (Bottom) Sum of ion current of *m/z* 73, 75, 117, and 147 ions.

trimethylchlorosilane (served as catalyst). Methylene chloride and acetonitrile (glass-distilled grade) were from EM Science (Gibbstown, NJ). Hexane (optimal grade) was from Fisher Scientific (Fairlawn, NJ).

Model Compound Studies. We have selected four types of model compounds bearing −COOH, −OH, and −C═O groups: (1) mono- and dicarboxylic acids; (2) hydroxy carboxylic acids; (3) oxocarboxylic acids; and (4) hydroxy carbonyls (Table 1). The model compounds are potential products from atmospheric oxidation of hydrocarbons. Model compounds containing carbonyl groups only are not included here, since their identification and detection by PFBHA derivatives have been described previously (*28*).

The model compounds prepared in acetonitrile were derivatized with 50 μL of 19 mM PFBHA acetonitrile/aqueous solution (a minimum amount of water was used to dissolve PFBHA·HCl). The mixture was allowed to stand at room-temperature overnight (16−24 h), before being blown to dryness under a gentle N_2 stream, followed by reconstitution with 100 μL of hexane and methylene chloride solvent (1:1) and addition of 20 μL of BSTFA. The mixture was then heated at 60 °C for 40 min. After cooling briefly, 1 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, then to 280 °C at 10 °C/min, and held at 280 °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

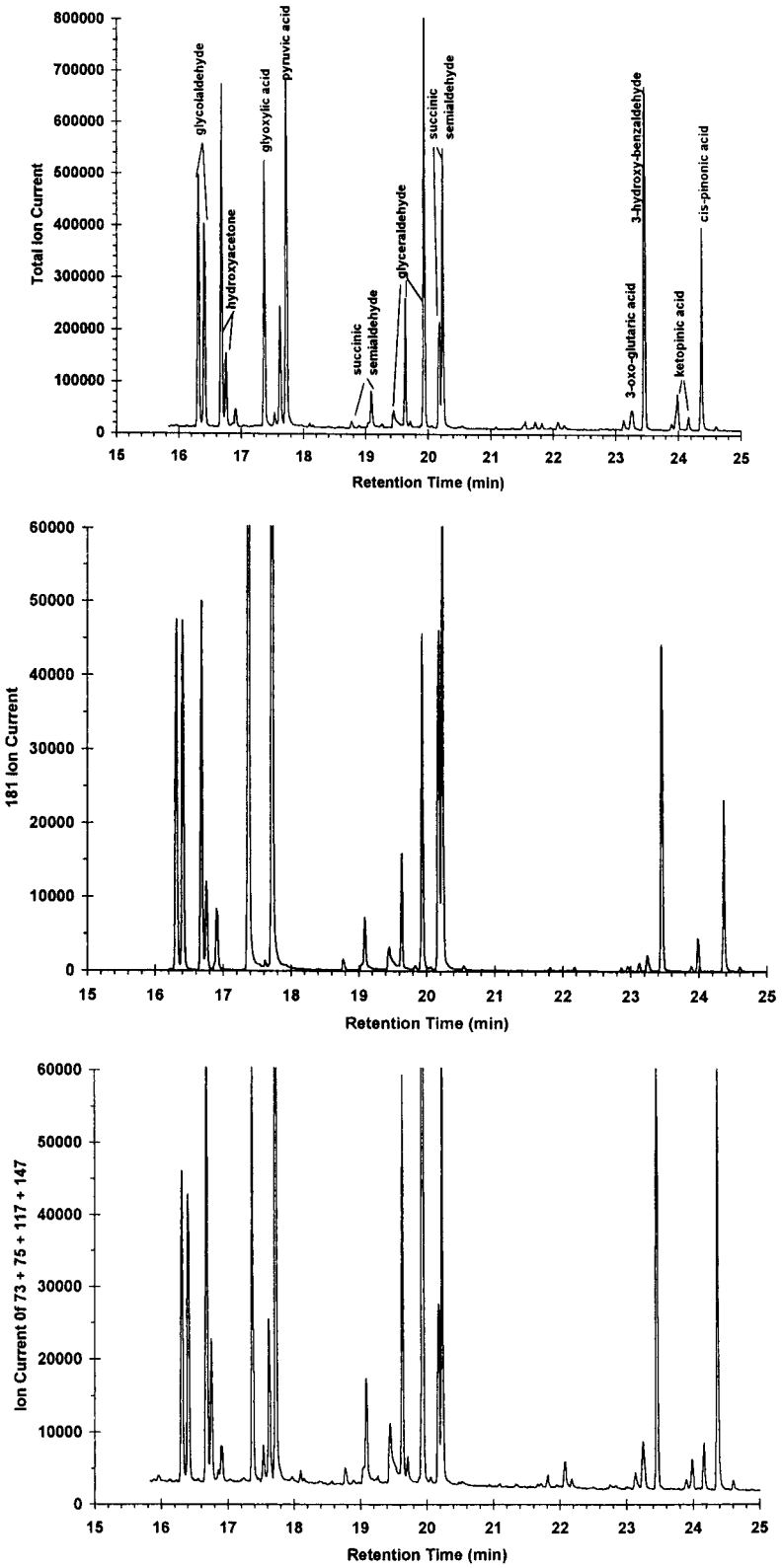


FIGURE 3. Chromatogram of a derivatized mixture of model compounds bearing −C═O and −COOH /OH groups. (Top) Total ion current. (Middle) *m/z* 181 ion current. (Bottom) Sum of ion current of *m/z* 73, 75, 117, and 147 ions.

at 60 °C for 1 min, then ramped to 250 °C at 180 °C/min, and held at 250 °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 was used for all samples.

Sample Collection and Treatment. Samples were collected from α-pinene/O_3 and Δ^3-carene/O_3 experiments, conducted in the dark in a 50 m^3 Teflon reactor which has been described previously (*29*). The reactor was heated during these experiments to 305−310 K, approximating the temperatures encountered during summer daytime. Initial concentrations of α-pinene and Δ^3-carene were 44 ppbv and 72 ppbv, respectively. 2-Butanol was also added at approximately twice the initial hydrocarbon concentration to scavenge OH radicals produced from the biogenic-O_3 reaction

TABLE 2. EI and CI Mass Spectra Patterns of Model Compound Derivatives

	% relative intensity (EI)							% relative intensity (CI)						
compd	73	75	117	147	181	M − 15	M	M + 181	M + 73	M + 1	M − 15	M − 89	M − 197	note
Group I: Mono- and Di- Carboxylic Acids														
hexanoic acid	64.6	98.1	61.6	0.2	–[a]	100.0	1.1	–	27.7	60.5	100.0	90.0	–	
heptanoic acid	54.3	82.4	72.4	1.6	–	100.0	2.0	–	28.3	72.3	100.0	88.1	–	
octanoic acid	55.4	77.3	89.2	0.6	–	100.0	3.2	–	72.4	95.7	100.0	87.1	–	
nonanoic acid	52.0	71.5	97.0	1.4	–	100.0	4.4	–	9.4	58.9	100.0	65.6	–	
benzoic acid	2.2	5.7	0.1	0.0	–	100.0	5.8	–	3.9	22.5	100.0	40.0	–	
p-toluic acid	3.2	8.7	2.5	0.2	–	100.0	6.4	–	6.2	28.2	100.0	44.4	–	
oxalic acid	51.7	4.0	0.9	100.0	–	5.3	0.1	–	28.1	47.8	15.5	0.0	–	100% = 73
malonic acid	20.8	9.0	0.6	100.0	–	12.5	1.9	–	12.6	100.0	13.0	39.0	–	
maleic acid	24.2	9.6	0.9	100.0	–	22.3	0.04	–	67.0	34.6	25.6	100.0	–	
succinic acid	20.9	15.5	0.5	100.0	–	24.4	2.3	–	56.5	12.7	34.6	100.0	–	
glutaric acid	35.8	32.1	3.8	100.0	–	65.4	1.1	–	64.3	5.5	35.6	100.0	–	
adipic acid	81.3	100.0	17.3	68.0	–	71.2	2.5	–	51.0	41.6	29.8	100.0	–	
Group II: Hydroxy Carboxylic Acids														
glycolic acid	42.6	4.8	1.2	100.0	–	21.2	0.3	–	23.2	4.7	33.1	0.0	–	100% = 367
lactic acid	78.2	10.7	41.1	100.0	–	13.0	0.4	–	53.7	4.7	26.9	0.3	–	100% = 191
Group III: Carboxylic Acids with a Carbonyl Group														
glyoxylic acid	29.8	5.5	3.0	0.0	100.0	24.3	5.4	20.8	22.0	77.5	32.3	20.5	14.2	100% = 73
pyruvic acid	59.5	6.9	4.6	0.2	100.0	36.5	8.8	11.7	14.6	82.6	26.0	46.8	0.0	100% = 73
ketomalonic acid	89.9	35.0	8.7	28.3	100.0	41.1	43.5	9.0	25.6	12.4	3.9	0.0	0.0	100% = 73
succinic semialdehyde	37.8	33.7	4.6	0.2	100.0	35.9	16.2	0.0	1.4	6.6	0.9	100.0	35.9	
oxalacetic acid	100.0	42.2	20.7	63.8	75.1	48.0	37.7	na[b]	100.0	21.0	4.4	0.8	0.0	
2-ketoglutaric acid	100.0	50.1	10.0	51.5	74.3	57.8	35.2	na[b]	18.6	9.6	5.8	2.2	2.7	100% = 73
3-oxoglutaric acid	100.0	29.6	6.4	26.9	51.1	54.1	17.8	na[b]	78.8	100.0	12.1	35.9	17.0	
cis-pinonic acid	100.0	31.9	5.9	2.1	52.3	0.6	1.1	0.0	15.2	100.0	0.0	7.4	11.0	
Group IV: Hydroxy Aldehydes and Ketones														
glycolaldehyde	32.1	9.3	4.2	0.0	51.3	100.0	0.6	36.9	6.1	44.8	100	41.9	28.5	
hydroxyacetone	62.4	16.6	5.8	0.4	56.6	100.0	1.5	17.2	0.0	100.0	98.7	81.7	88.9	
glyceraldehyde	78.2	8.5	7.6	37.3	33.9	10.8	0.3	4.7	0.0	23.1	12.8	47.0	0.0	100% = M − 211
3-hydroxy-benzaldehyde	47.2	8.3	3.5	0.4	43.6	23.8	100.0	2.7	0.0	79.1	3.9	0.0	100.0	

[a] Not observed due to absence of aldehyde or ketone groups. [b] na, not applicable due to being out of available mass range.

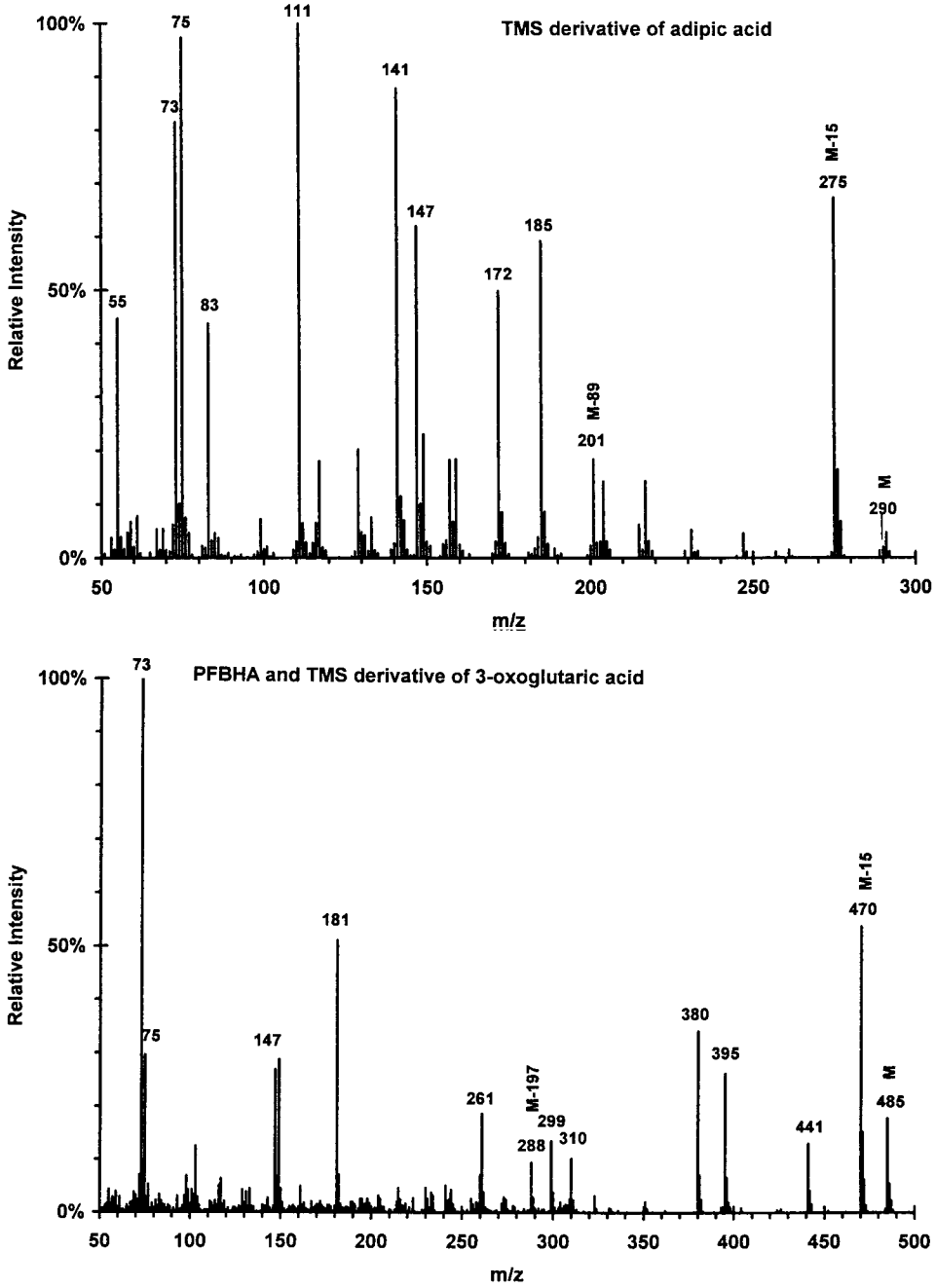


FIGURE 4. EI mass spectra of derivatized adipic acid and 3-oxoglutaric acid.

(*2, 30*). Finally, ozone was added to the reactor until its concentration reached approximately four times that of the initial hydrocarbon. As a result of excessive ozone, the hydrocarbon was consumed entirely at the end of an experiment. Reactor air was pulled through a 0.5 m × 8 mm i.d. Teflon line and passed through an impinger (with frits) containing 200 mL of acetonitrile solvent at a flow rate of about 2 L/min for 3 h. No ice bath was used to reduce the evaporation of collection solvent. At the end of the 3 h sampling, 200 mL of acetonitrile was reduced to about 100 mL. Immediately after collection of a sample, 50 μL of 19 mM PFBHA acetonitrile/aqueous solution was added, and the mixture was allowed to react overnight before it was reduced to about 5 mL by rotary evaporation. The sample was then blown to dryness under a stream of N_2, reconstituted, and derivatized with BSTFA as described for those model compounds.

Results and Discussion

Derivatization Conditions and GC Separation. The reaction time for the derivatization of carbonyl groups with PFBHA is chosen to be between 16 and 24 h for convenience and completeness of reaction (*24, 31*). At room temperature, the model compounds require 6 h to complete the silylation reactions. At an elevated temperature of 60 °C, the reactions take only 40 min to complete.

The PFBHA and TMS derivatives are well resolved on a commonly used DB-5 GC capillary column. Figure 2 shows a GC chromatogram of the TMS derivatives of standards bearing one or more of OH/COOH groups (groups I and II compounds in Table 1). Figure 3 shows a GC chromatogram of double derivatized oxocarboxylic acids and hydroxy carbonyls (groups III and IV compounds in Table 1). All the compounds are well-separated and exhibit good peak shapes. PFBHA derivatives often show multiple peaks for a non-

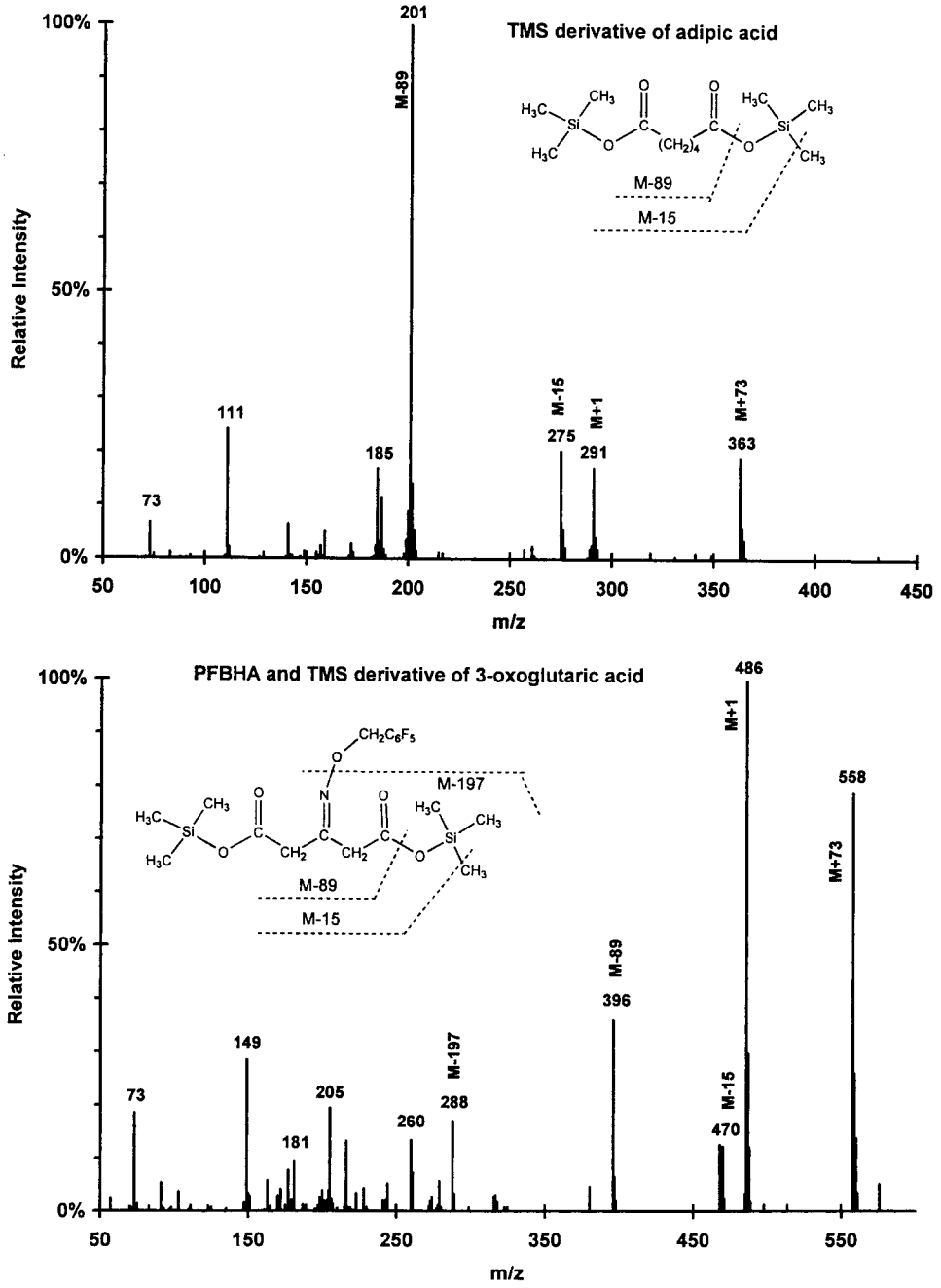


FIGURE 5. CI mass spectra of derivatized adipic acid and 3-oxoglutaric acid.

symmetric parent carbonyl because PFBHA forms two geometric isomers due to the nitrogen−carbon double bond, and the isomers can often be resolved by a GC column (*24, 28*).

EI Mass Spectra of Model Compounds. The derivatives share several common ion fragments resulting from the moieties that come from the derivatizing agents. Table 2 compiles a list of these fragments and their relative abundance. For all compounds containing −OH and −COOH groups, substitution of the active H atom in −OH and −COOH function groups with $Si(CH_3)_3$ gives rise to common ion fragments at m/z 73 and 75, $[Si(CH_3)_3]^{\bullet+}$ and $[HO{=}Si(CH_3)_2]^{\bullet+}$, respectively. In addition, monocarboxylic acids show a strong fragment at m/z 117, i.e., $[COOSi(CH_3)_3]^{\bullet+}$, a moiety resulting from the TMS group and acid functionality; for compounds with two active H atoms such as dicarboxylic acids, hydroxy carboxylic acids, and dihydroxy aldehydes, the m/z 147 ion, postulated as $[(CH_3)_2Si{=}OSi(CH_3)_3\_]^{\bullet+}$ (*32*), is very strong, with relative intensity (RI) ranging from 15 to 100%. As a result, ions 73, 75, 117, and 147 can be used to differentiate compounds bearing −OH and −COOH from other classes of organics. Figure 2 shows the GC chromatogram of the TMS derivatives of carboxylic acids and hydroxy carboxylic acids, along with pentadecane. The select ion chromatogram for ions 73, 75, 117, and 147 shows peaks for each TMS derivative, but not pentadecane. This demonstrates that these common fragments can serve as indicators of the presence of −OH or −COOH functionality. A strong m/z 147 ion may be used to postulate the presence of two of −OH and −COOH groups.

For compounds containing carbonyl group(s), the conversion of such groups to $C{=}NOCH_2C_6F_5$ renders the resulting derivatives a strong fragment ion at $m/z = 181$, $[C_6F_5\,CH_2]^+$, RI ranging from 34 to 100% (Table 2). Therefore the 181 ion can be used to identify compounds bearing carbonyl groups from the rest of a mixture. Figure 3 shows that, for each

TABLE 3. Pseudomolecular Ions of PFBHA and TMS Derivatives in Their Methane Chemical Ionization Mass Spectra

PFBHA derivatives		TMS derivatives	
ion	fragment	ion	fragment
M + 181	$[M + C_6F_5CH_2]^{\bullet+}$	M + 73	$[M + Si(CH_3)_3]^{\bullet+}$
M + 1	$[M + H]^+$	M + 1	$[M + H]^+$
M − 181	$[M - C_6F_5CH_2]^{\bullet+}$	M − 15	$[M - CH_3]^{\bullet+}$
M − 197	$[M - C_6F_5CH_2O]^{\bullet+}$	M − 89	$[M - OSi(CH_3)_3]^{\bullet+}$

compound with both carbonyl and carboxy/hydroxy groups, the 181 ion chromatogram has a corresponding peak and that the 73 + 75 + 117 + 147 ion chromatogram also has a corresponding peak. In addition to serving as indicators, the strong intensity of these common ion fragments makes them suitable for quantitation. Two EI mass spectra are given in Figure 4, using adipic acid and 3-oxoglutaric acid as examples.

Molecular ions of TMS derivatives of carboxylic acids without a carbonyl group are weak or nonexistent (RI ranging from 0 to 6%) in their EI mass spectra. For carboxylic acids with carbonyl functionality, both carbonyl and acid groups are derivatized. The resulting derivatives show molecular ions of moderate intensity (RI 1−55%). For hydroxy aldehydes and ketones, their double derivatized forms exhibit low molecular ion intensity (RI 0.3−1.5%), 3-hydroxy benzaldehyde being an exception probably as a result of the presence of a benzene-ring functionality. A pseudomolecular ion at m/z M − 15, resulting from loss of a methyl group from the neutral molecule, is prominent in EI spectra for every standard examined (5−100%), *cis*-pinonic acid being an exception. The loss of a methyl group is so favored for TMS derivatives of monocarboxylic acids that the M − 15 ion

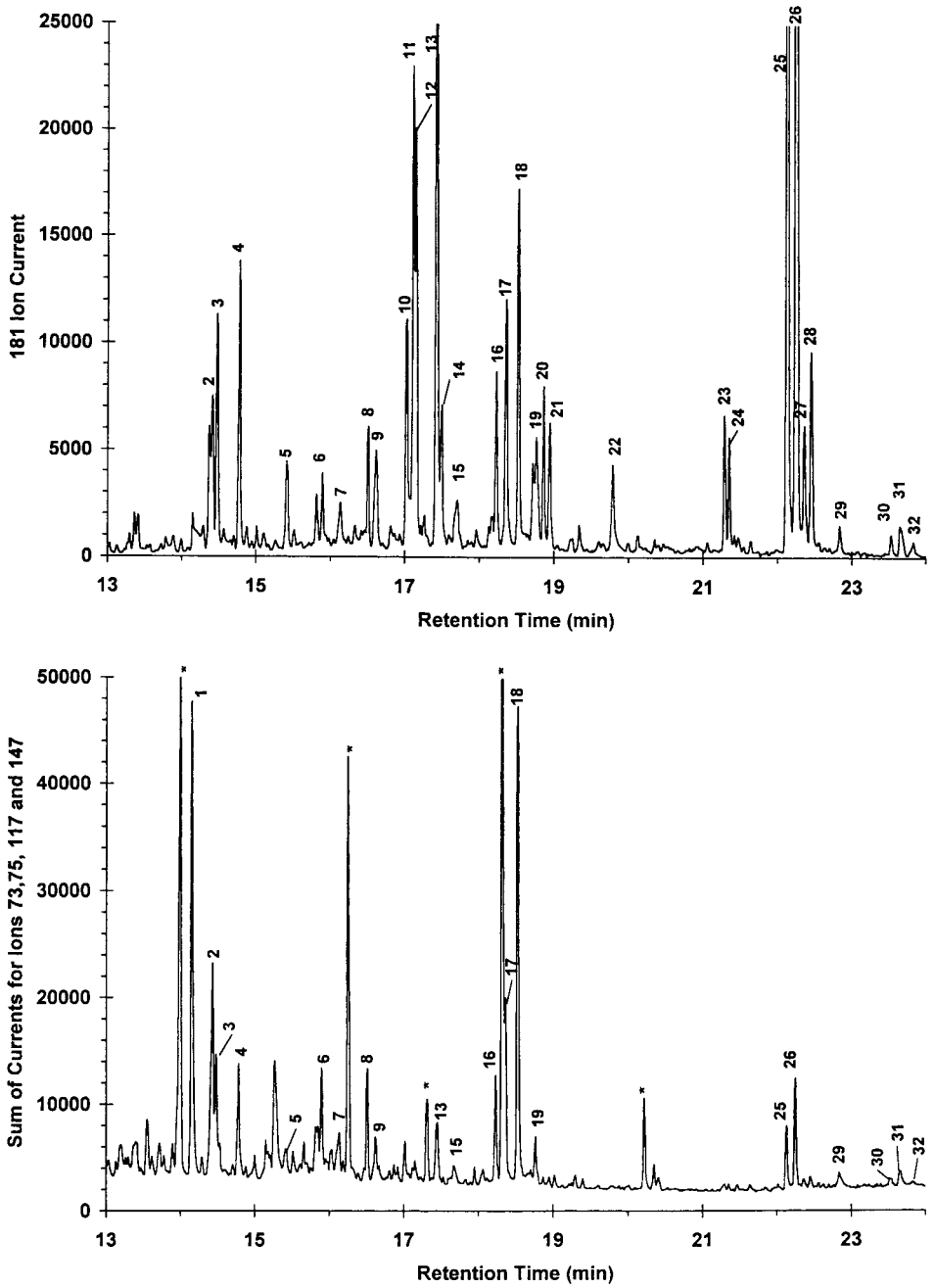


FIGURE 6. Chromatograms of products from α-pinene/O_3 reaction system, see Table 4 for peak identification. (Top) Products bearing −C═O groups. (Bottom) Products bearing −COOH or −OH groups. [(*) *n*-Alkanoic acids, present in concentrated acetonitrile solvent.]

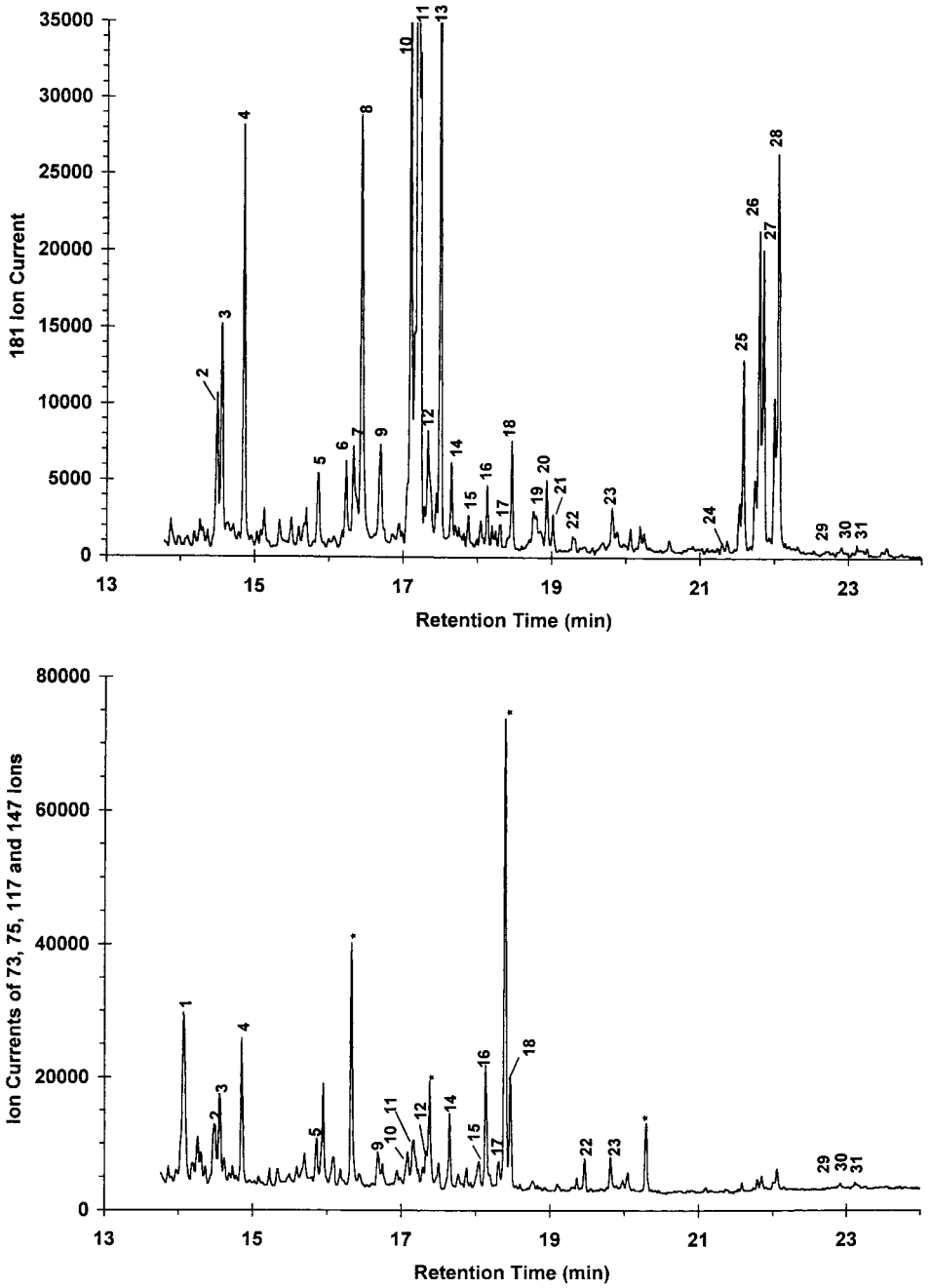


FIGURE 7. Chromatograms of products from Δ^3-carene/O_3 reaction system, see Table 5 for peak identification. (Top) Products bearing −C═O groups. (Bottom) Products bearing −COOH or −OH group. [(*): *n*-Alkanoic acids, present in concentrated acetonitrile solvent.]

dominates the spectra. While this ion can aid the determination of molecular weight, it alone does not provide a confident diagnosis.

Methane CI Mass Spectra of Model Compounds. Table 2 lists the CI mass spectra data of model PFBHA/TMS derivatives. As illustrations, Figure 5 shows the full CI mass spectra of the TMS derivative of adipic acid, and the PFBHA and TMS derivative of 3-oxoglutaric acid. PFBHA derivatives are known to have several pseudomolecular ions of strong relative intensity in their methane CI mass spectra (*28*). These ions are listed in Table 3. TMS derivatives of carboxylic acids and hydroxy carboxylic acids also exhibit a number of pseudomolecular ions in their methane CI mass spectra with strong intensity (Table 3). When both −COOH (or −OH) and −C═O are present in a compound, one observes pseudomolecular ions characteristic of the two different types of functional groups in the original molecules.

The adduct ions $[(M + 181)^+]$ and $[(M + 73)^+]$ result from a special principle of the ion trap mass spectrometer. In the ion trap mass spectrometer, the ion source and the mass analyzer are combined as one piece of hardware. A radio frequency field is scanned upward to eject ions of increasing mass-to-charge ratio for detection. Before the ions are ejected, secondary ion−molecule reactions are possible. For the derivatives examined here, fragment ions at m/z 181 and 73 are abundant in the trap, and they have time to form ion adducts with neutral molecules before they are ejected out the trap. Ions with m/z M − 181, M − 197, M − 15, and M − 89 result from loss of $C_6F_5CH_2$, $C_6F_5CH_2O$, CH_3, and $OSi(CH_3)_3$, respectively, from the neutral molecules. For each model compound examined, three or more pseudomolecular ions listed in Table 3 are observed to have RI > 4%, as shown in Table 2. The multiple pseudomolecular ions make it possible to reliably determine molecular weights for unknown

TABLE 4. Products from α-Pinene/O_3 Reaction System

peak no. in Figure 6	*RT* (min)	derivative MW	original MW	C=O	OH or COOH	identification
1	14.14	330	186		x[a]	pinic acid[c]
2, 3	14.38, 14.48	369	102	x	x	succinic semialdehyde[c,d]
4	14.78	383	116	x	x	C_5 oxoacid[b,d]
5	15.41	367	100	x	x	C_4 unsaturated oxoacid[b]
6, 7	15.90, 16.13	457	118	x	x	C_4 hydroxy oxoacid[b]
8	16.49	423	156	x	x	G in Table 6[b]
9	16.61	397	130	x	x	C_6 oxoacid[b]
10	17.01	448	58	x		glyoxal[c,d]
11	17.11	462	72	x		methylglyoxal[c]
12	17.14	448	58	x		glyoxal[c,d]
13	17.43	462	72	x		methylglyoxal[c]
13	17.43	437	170	x	x	norpinonic acid[b]
14	17.49	573	183	x		unknown
15	17.66	437	170	x	x	norpinonic acid[b]
16, 17	18.21,18.36	437	170	x	x	D_2 in Table 6[b]
18, 19	18.53, 18.76	451	184	x	x	pinonic acid[c]
19	18.76	476	86	x		C_4 saturated dicarbonyl[b]
20, 21	18.86, 18.94	490	100	x		C_5 saturated dicarbonyl[b]
22	19.78	502	112	x		C_6 unsaturated dicarbonyl[b]
23, 24	21.26, 21.34	544	154	x		norpinonaldehyde[b]
25, 26	22.13, 22.24	558	168	x		pinonaldehyde[b]
27, 28	22.34,22.44	558	168	x		pinonaldehyde[b]
29, 30	22.83,23.53	646	184	x	x	$C_{10}H_{16}O_3$, F in Table 6[b]
31, 32	23.64, 23.81	646	184	x	x	$C_{10}H_{16}O_3$, F in Table 6[b]

[a] x denotes presence of a functional group. [b] Tentatively identified based on EI and CI mass spectra. [c] Confirmed with an authentic standard. [d] Present in concentrated acetonitrile solvent blank.

TABLE 5. Products from Δ^3-Carene/O_3 Reaction System

peak no. in Figure 7	*RT* (min)	derivative MW	original MW	C=O	OH or COOH	identification
1	14.10	330	186		x[a]	$C_9H_{14}O_4$, E′ in Table 6[b]
2, 3	14.49, 14.55	369	102	x	x	succinic semialdehyde[c,d]
4	14.84	383	116	x	x	C_5 oxoacid[b,d]
5	15.84	411	144	x	x	C_7 oxoacid[b]
6	16.23	351	156	x		C_{10} carbonyl[b]
7, 8	16.33, 16.45	337	142	x		C_9 carbonyl[b]
9	16.69	397	130	x	x	C_6 oxoacid[b]
10	17.06	437	170	x	x	norcaronic acid[b]
10	17.09	448	58	x		glyoxal[c,d]
11	17.19	462	72	x		methylglyoxal[c]
11	17.19	448	58	x		glyoxal[c,d]
11, 12	17.16, 17.36	423	156	x	x	G′ in Table 6[b]
12	17.38	437	170	x	x	norcaronic acid or D′$_2$ in Table 6[b]
12, 13	17.33, 17.49	462	72	x		methylglyoxal[c]
14	17.64	437	170	x	x	norcaronic acid or D′$_2$ in Table 6[b]
15	17.88	435	168	x	x	$C_9H_{12}O_3$[b]
16	18.13	451	184	x	x	caronic acid[b]
17	18.31	437	170	x	x	D′$_2$ in Table 6[b]
18	18.46	451	184	x	x	caronic acid[b]
19, 21	18.76, 18.93, 19.01	490	100	x		C_5 saturated dicarbonyl[b]
22	19.29	550	88	x	x	C_3 hydroxy dicarbonyl[b]
23	19.81	539	200	x	x	C_{10} hydroxy oxoacid[b]
24	21.29	544	154	x		norcaronaldehyde[b]
25, 26	21.58, 21.79	558	168	x		caronaldehyde[b]
27, 28	22.84, 22.04	558	168	x		caronaldehyde[b]
29−31	22.73, 22.96, 23.11	646	184	x	x	$C_{10}H_{16}O_3$, F′ in Table 6[b]

[a] x denotes presence of a functional group. [b] Tentatively identified based on EI and CI mass spectra. [c] Confirmed with an authentic standard. [d] Present in concentrated acetonitrile solvent blank.

compounds. In addition, unlike EI spectra that often exhibit numerous fragment ions (Figure 4), CI mass spectra show fewer fragments, making identification easier.

Detecting and Identifying Products from O_3 Oxidation of α-Pinene and Δ^3-Carene. Using combined PFBHA/BSTFA derivatization, we have detected a number of products from the O_3 oxidation of α-pinene and Δ^3-carene. The presence of carbonyl-containing products was readily determined by examination of the reconstructed ion chromatogram for m/z 181, whereas the presence of products bearing hydroxyl and carboxyl groups was determined by the reconstructed ion chromatogram for m/z 73, 75, 117, and 147 (Figures 6 and 7). Tables 4 and 5 list the products shown in Figures 6 and 7. Many of the products have more than one polar functional groups. The PFBHA derivative of pinonaldehyde shows peaks (peaks 25 and 26) in the bottom chromatogram in Figure 6, where they are not expected, as pinonaldehyde is a C_{10} dicarbonyl without a COOH/OH group. A close examination

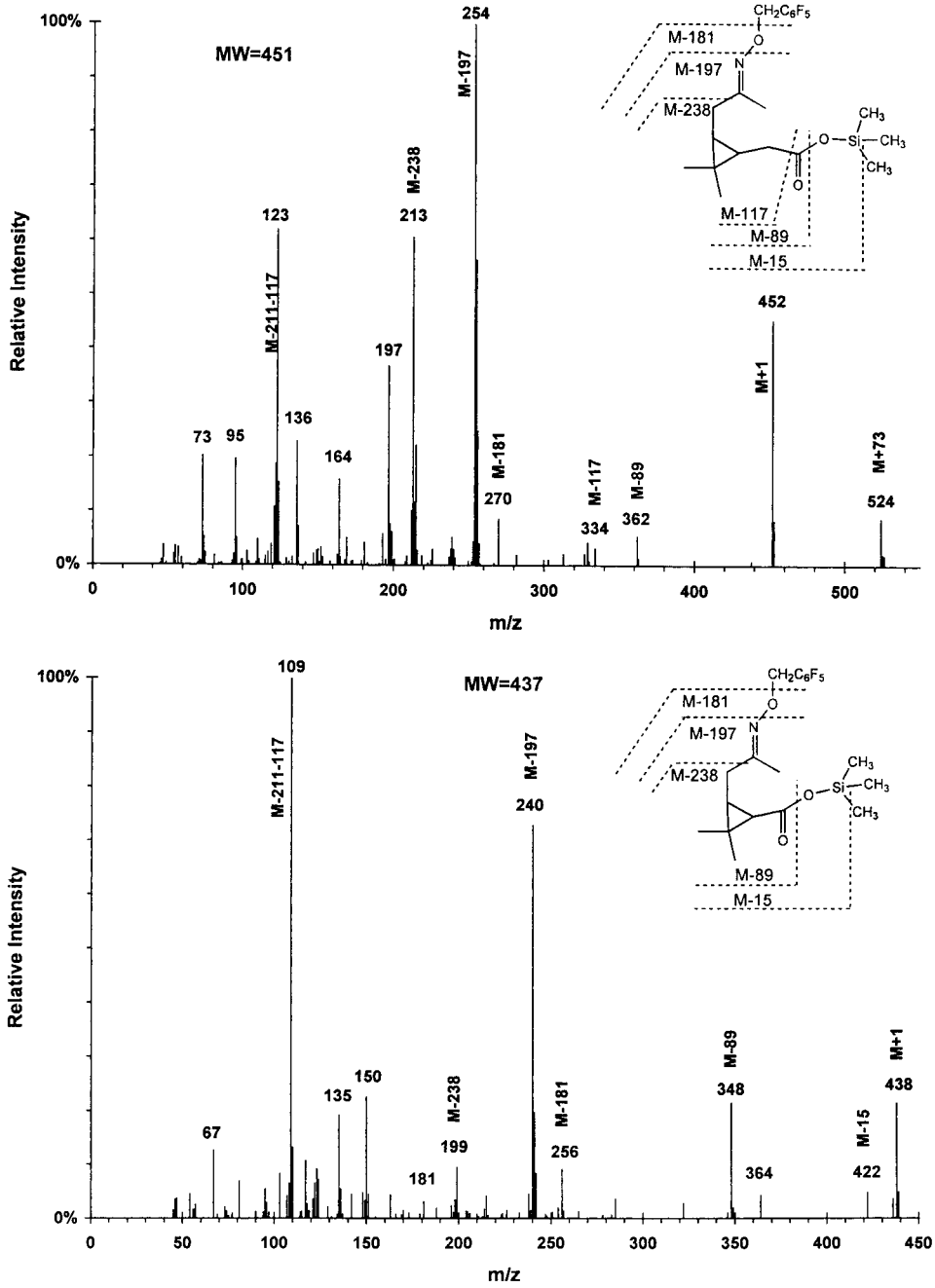


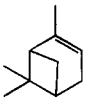
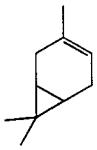
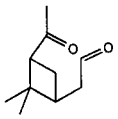
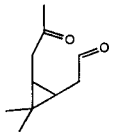
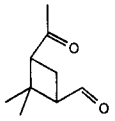
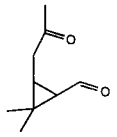
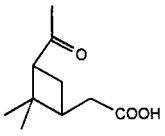
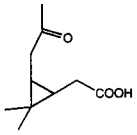
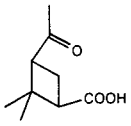
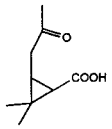
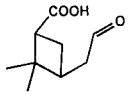
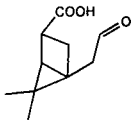
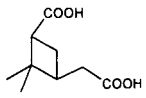
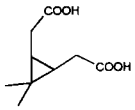
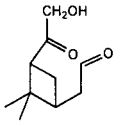
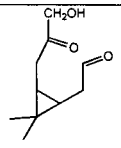
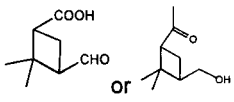
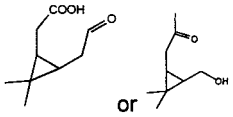
FIGURE 8. Methane chemical ionization mass spectra of two double-derivatized products from Δ^3-carene/O_3 reaction. (Top) Caronic acid. (Bottom) Norcaronic acid.

of the EI mass spectra showed that ions at *m*/*z* 73, 75, 117, and 147 have low relative intensity, unlike those with the TMS moiety that results in these ions of strong intensity. Ions at *m*/*z* 73, 75, 117, and 147, along with many other small ion fragments, were generated as a result of the high concentration of the pinonaldehyde-PFBHA derivative in the sample.

The molecular weights of most compounds are easily determined by interpretation of their EI and CI mass spectra. For example, Figure 8 shows the CI mass spectra of the derivatives of two products, caronic acid and norcaronic acid, from the Δ^3-carene/O_3 reaction, illustrating the determination of molecular weights and some structural moieties.

Among biogenic hydrocarbons, α-pinene is the most frequently studied monoterpene for its atmospheric chemistry. At an initial α-pinene mixing ratio of several parts per million by volume, pinonaldehyde has been clearly identified as a major product (*33*−*36*); Hatakeyama et al. (*33*) also identified norpinonaldehyde, pinonic acid, and norpinonic acid as oxidation products. In a study conducted with mixing ratios of α-pinene at several hundred parts per million by volume, additional products, α-pinene epoxide, and three C_{10} hydroxy dicarbonyls were reported (*37*). Table 6 lists the structures of these products from O_3 oxidation of α-pinene. In our experiment conducted with an initial α-pinene concentration of 0.044 ppmv, all of the above products, with the exception of α-pinene epoxide, which does not have either a C═O or an OH/COOH group, were observed using the PFBHA/BSTFA derivatization technique. We also detected three additional products. The first was identified as pinic acid, a C_9 dicarboxylic acid (peak 1 in Figure 6, see Table 6 for its structure), from the EI and CI mass spectra of its TMS derivative. The identification was confirmed by comparison with an authentic standard obtained from Aldrich. The

TABLE 6. Products from Ozone Oxidation of α-Pinene and Δ^3-Carene

α-Pinene 	Δ^3-Carene 
A: $C_{10}H_{16}O_2$ pinonaldehyde MW=168 Deri. MW=558 	A' MW=168 Deri. MW=558 
B:$C_9H_{14}O_2$ norpinonaldehyde MW=154 Deri. MW=544 	B':$C_9H_{14}O_2$ norcaronaldehyde MW=154 Deri. MW=544 
C:$C_{10}H_{16}O_3$ pinonic acid MW=184 Deri. MW=451 	C':$C_{10}H_{16}O_3$ caronic acid MW=184 Deri. MW=451 
D_1:$C_9H_{14}O_3$ norpinonic acid MW=170 Deri. MW=437 	D_1':$C_9H_{14}O_3$ norcaronic acid MW=170 Deri. MW=437 
D_2:$C_9H_{14}O_3$ MW=170 Deri. MW=437 	D_2':$C_9H_{14}O_3$ MW=170 Deri. MW=437 
E:$C_9H_{14}O_4$ pinic acid MW=186 Deri. MW=330 	E':$C_9H_{14}O_4$ MW=186 Deri. MW=330 
F:$C_{10}H_{16}O_3$ MW=184 Deri. MW=646  and isomers	F':$C_{10}H_{16}O_3$ MW=184 Deri. MW=646  and isomers
G $C_8H_{12}O_3$ or $C_9H_{16}O_2$ MW=156 Deri. MW=423 	G' $C_8H_{12}O_3$ or $C_9H_{16}O_2$ MW=156 Deri. MW=423 

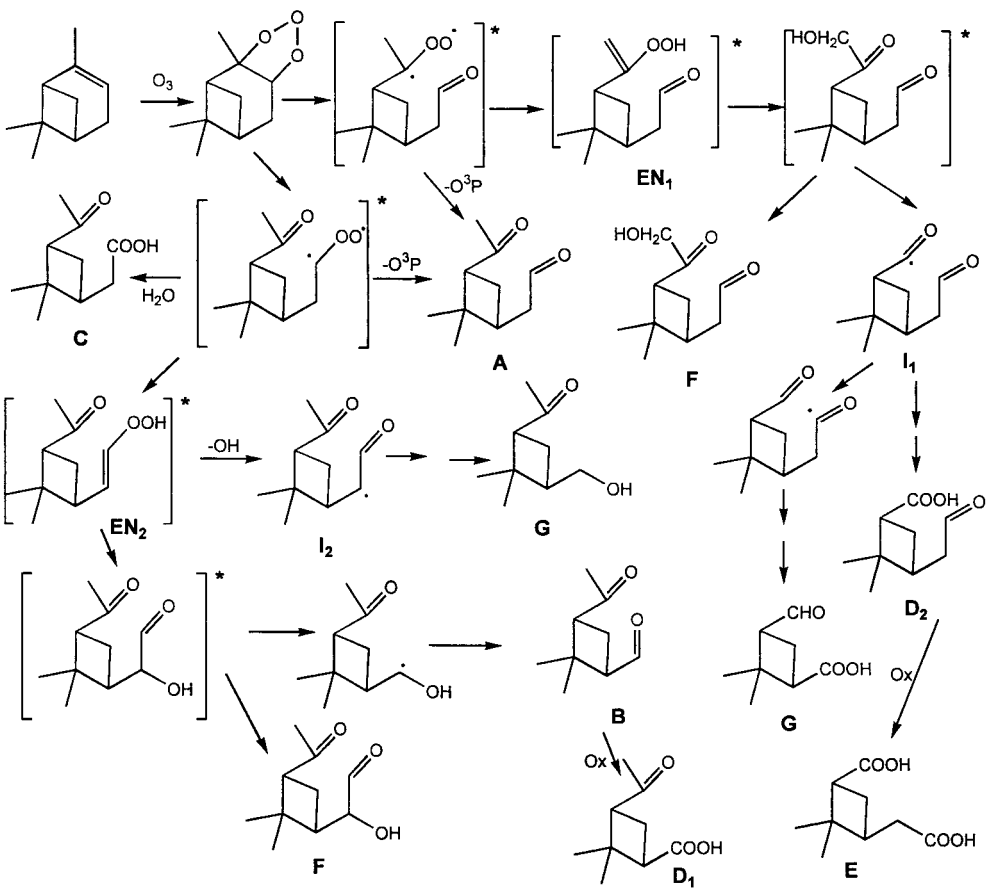


FIGURE 9. Mechanism for the α-pinene/O_3 reactions. (*) Energy-rich species. The marked letters correspond to those in Table 6.

second was identified as 2,2-dimethyl-3-(formylmethyl)-cyclobutane-formic acid (peaks 16 and 17 in Figure 6, D_2 in Table 6), an isomer of norpinonic acid (D_1 in Table 6). The third has a molecular weight of 156 (peak 8 in Figure 6) and contains both a carbonyl group and a COOH/OH group, as indicated by its EI and CI mass spectra. This product could be 1-acetyl-2,2-dimethyl-3-hydroxymethyl-cyclobutane, or 2,2-dimethyl-3-formyl-cyclobutane-formic acid (G in Table 6). The second possible structure is similar to but having one fewer carbon atom than norpinonicacid. Distinguishing further between the two possibilities is not possible based on the EI and CI spectra.

At the present, mechanistic pathways for the formation of these products are largely speculative. On the basis of known reaction mechanisms for alkene-O_3 reactions, it is possible to propose a reaction scheme, shown in Figure 9, to account for the observed products. The reaction of α-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 two biradicals. The observed products are formed from the subsequent reactions of the two biradicals. The energy-rich biradicals can be collisionally stabilized. The reaction of water with one of the stabilized biradicals leads to pinonic acid (C). Elimination of $O(^3P)$ from either of the two biradicals gives rise to pinonaldehyde (A). This channel, however, accounts for only a small fraction of pinonaldehyde formed, as $O(^3P)$ formation yield is less than 3% (*2*). As the amount of 2-butanol used in the experiment was insufficient to scavenge all OH radicals, a fraction of pinonaldehyde likely results from OH-initiated oxidation of α-pinene (*33*). The formation of C_{10} hydroxy dicarbonyls (F) is postulated to result from the Criegee radicals via a hydroperoxide channel, i.e., Criegee radicals isomerization to enehydroperoxides through intramolecular hydrogen migration, and the subsequent isomerization to hydroxy dicarbonyls (*2, 9*−*11*). The decomposition of enehydroperoxides leads to products with fewer carbons than the parent Criegee radicals. This may account for the formation of norpinonaldehyde (B) and D_2. The formation of norpinonic acid (D_1) and pinic acid (E) is presupposed to result from oxidation of their corresponding aldehydes, norpinonaldehyde, and D_2, respectively. However, the explicit mechanism is unclear. The two possible candidates for G are postulated to arise from decomposition of intermediates I_1 and I_2. I_1 results from decomposition of enehydroperoxide EN_1, and the loss of an OH radical from enehydroperoxide EN_2 produces I_2 (*2*).

Two product studies of Δ^3-carene oxidation are available in the literature (*34, 35*). Only one product, 2,2-dimethyl-3-(2-oxopropyl)-cyclopropaneacetaldehyde or caronaldehyde (name derived as an analogy to pinonaldehyde), has been clearly identified. As shown in Figure 7, we have detected products in addition to caronaldehyde. Since Δ^3-carene and α-pinene both have an internal unsaturated bond where O_3 oxidation takes place (see Table 6 for their structures), one expects that this structural similarity would lead to similar oxidation products. In addition to listing the products observed from α-pinene/O_3 reactions, Table 6 shows the corresponding products from Δ^3-carene/O_3. These analogous products are all tentatively identified (Figure 7 and Table 5).

Pinonaldehyde, norpinonaldehyde, pinonic acid, and norpinonic acid have been reported to be particulate products from α-pinene oxidation (*33, 38*). Considering that pinic acid and D_2 have lower volatility than the above-known aerosol phase products, one would not be surprised to find them in the aerosol phase. Similarly, the corresponding products from Δ^3-carene can be expected to contribute also to aerosol formation. The products identified in this work suggest that compounds with multiple polar functional groups are components of secondary organic aerosols. This

conclusion is consistent with the previous FTIR studies of functionality distribution for secondary organic aerosols (*16*−*18*).

Quantitative determination is possible for products that have standards available. We have not attempted to quantify the products, as most of them do not have readily available standards. On the basis of our preliminary work, we estimate that the method can detect in the parts per trillion by volume range for a collection volume of 300 L of air if we assume a 100% collection efficiency, a 100% derivatization efficiency, and no loss in the sample evaporation process.

Acknowledgments

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