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Analysis of Airborne Carboxylic Acids and Phenols as Their Pentafluorobenzyl Derivatives: Gas Chromatography/Ion Trap Mass Spectrometry with a Novel Chemical Ionization Reagent, PFBOH

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The complex photochemical transformations of biogenic hydrocarbons such as isoprene and of anthropogenic hydrocarbons such as aromatics are an important source of carboxylic acids in the troposphere. The identification of unknown carboxylic acids can be difficult, however, due to the lack of standards as well as poor sensitivity and lack of selectivity of existing techniques. In this study, we describe the development of a method to analyze airborne carboxylic acids using derivatization with pentafluorobenzyl bromide (PFBBr) followed by capillary gas chromatography/ion trap mass spectrometry (GC/ITMS) analysis. In addition to the typical electron impact ionization (EI) and methane chemical ionization (CI) mass spectra of pentafluorobenzyl derivatives, we describe the use of pentafluorobenzyl alcohol (PFBOH) as a novel reagent gas for CIMS. Pentafluorobenzyl ions ($m/z = 181$) were produced at reduced pressure (1×10^{-5}−2×10^{-5} Torr) from PFBOH gas, and the resulting CIMS were characterized by the predominance of the $[M + 181]^+$ ions. The carboxylic acid products in the oxidation of isoprene from indoor and outdoor smog chamber experiments were analyzed using the described PFBBr GC/ITMS method. The formation of methacrylic acid in an isoprene/O_3 reaction was demonstrated experimentally for the first time, and acrylic acid, one of the U.S. EPA 189 Hazardous Air Pollutants, is first reported here as an isoprene oxidation product. In other outdoor toluene/NO_x chamber experiments, we detected a series of carboxylic acids and various phenolic compounds using this method.

Introduction

Carboxylic acids are ubiquitous throughout the troposphere (*1, 2*), and numerous studies have shown that some organic acids, including formic and acetic acids, can contribute a significant fraction (25−98%) of the natural acidity in precipitation and cloudwater in many parts of the world (*3*−*5*). These acids are emitted into the atmosphere from various sources; in addition to primary emissions from anthropogenic and biogenic sources, the photochemical transformations of several precursors to carboxylic acids in the atmosphere is also important (*6*−*8*). Laboratory and field investigations indicate that atmospheric carboxylic acids can be produced via oxidation of organic hydrocarbons and aldehydes by oxidants (e.g., ozone) and various free radicals (e.g., $^{\bullet}OH$, $HO_2^{\bullet}$). For instance, significant sources of carboxylic acids in the ambient atmospheric environment are aqueous-phase oxidation of aldehydes by hydroxyl radical in cloudwater or rainwater (*9*−*12*) and the ozone−alkene reaction (*13*, *14*).

In recent years, there has been considerable interest in characterizing products arising from the photooxidation of isoprene and aromatics in studies to elucidate chemical reaction mechanisms affecting tropospheric ozone formation. Because of their large-scale emissions (isoprene has the second largest flux of all hydrocarbons, and the aromatics are abundant components in automobile emissions) and high reactivity, isoprene and aromatics can have a significant impact on ozone formation. The complexity of the atmospheric oxidation of isoprene and aromatics, however, has made the explicit description of their chemistry quite difficult. Because there are multiple possibilities for carboxylic acid formation in isoprene and aromatics oxidation, especially for species like formic acid, determining the actual mechanistic pathway is difficult. Although several chemical mechanisms have been postulated for the formation of carboxylic acids (*15*−*17*), we lack sufficient knowledge regarding the identity of the complement of carboxylic acids generated to elucidate complete reaction pathways. Progress in understanding the oxidation chemistry has been deterred due to the lack of specific and sensitive detection techniques capable of identifying acid intermediates.

The analytical techniques previously employed to measure airborne carboxylic acids include ion chromatography (IC) by ion exchange or ion exclusion, liquid chromatography (LC) (*18*−*22*), and gas chromatography (GC). Derivatization methods in combination with LC and GC have also been utilized (*23*). Although direct IC and LC methods are simple and inexpensive to use, poor resolution and the necessity for authentic standards for identification of compounds by matching retention times are significant limitations to these techniques. GC analysis of free carboxylic acids requires either special column phases (*24*) or derivatization. Several derivatization reagents, including methylformate (*25*) and pentafluorobenzyl bromide (PFBBr), have been utilized with GC (*26*−*32*). We were attracted to the employment of PFBBr because of the success encountered with pentafluorobenzylhydroxyl amine (PFBHA), a structurally similar reagent, with chemical ionization mass spectrometry (CIMS) to identify airborne carbonyls (*33*−*36*). In addition, derivatives of compounds with various functional groups, including carboxylic acids, phenols (Scheme 1), amines, and mercaptans, can be formed allowing the identification of several classes of molecules with excellent yields (*37*).

The resulting derivatives are stable and amenable to gas chromatographic separation, after which mass spectrometry detection greatly improves the selectivity and sensitivity of the method. Recently, structural analyses of these pentafluorobenzyl derivatives were described with GC/MS using electron-impact (EI) or electron capture negative ion-

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SCHEME 1. Derivatization of Carboxylic Acids and Phenols to Respective Esters and Ethers

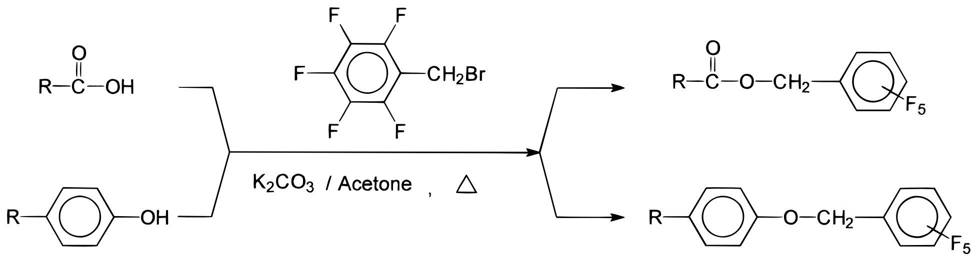


TABLE 1. PFBBr Derivatives of Selected Model Compounds and Their GC Properties

PFB derivative of	MW[a]	structure	RRT[b]	RRF[c]
		Monoalkanoic Acids		
formic acid	226	$HC(O)OCH_2C_6F_5$	−0.23	1.00
acetic acid	240	$CH_3C(O)OCH_2C_6F_5$	1.27	0.88
propionic acid	254	$CH_3CH_2C(O)OCH_2C_6F_5$	3.04	0.95
butanoic acid	268	$CH_3(CH_2)_2C(O)OCH_2C_6F_5$	4.67	0.66
valeric acid	282	$CH_3(CH_2)_3C(O)OCH_2C_6F_5$	6.42	0.47
hexanoic acid	296	$CH_3(CH_2)_4C(O)OCH_2C_6F_5$	8.12	0.37
		Alkenoic Acids		
acrylic acid	252	$CH_2{=}CHC(O)OCH_2C_6F_5$	2.89	0.59
methacrylic acid	266	$CH_2{=}C(CH_3)C(O)OCH_2C_6F_5$	4.35	0.46
vinylacetic acid	266	$CH_2{=}CHCH_2C(O)OCH_2C_6F_5$	4.48	ND[d]
trans-crotonic acid	266	$CH_3CH{=}CHC(O)OCH_2C_6F_5$	5.72	ND
		Hydroxy Acids		
glycolic acid	256	$HOCH_2C(O)OCH_2C_6F_5$	5.15	0.40
		Oxocarboxylic Acids		
pyruvic acid	268	$CH_3C(O)C(O)OCH_2C_6F_5$	4.82	0.28
4-oxopentanoic acid	296	$CH_3C(O)(CH_2)_2C(O)OCH_2C_6F_5$	9.49	0.23
		Aromatic Acids		
benzoic acid	302	$C_6H_5C(O)OCH_2C_6F_5$	11.75	0.24
hydroxybenzoic acid	498[e]	$HOC_6H_4C(O)OCH_2C_6F_5$	23.55	0.68
		Diacids		
maleic acid	476[e]	$C_6F_5CH_2O(O)CCH{=}CHC(O)OCH_2C_6F_5$	17.07	ND
succinic acid	478[e]	$C_6F_5CH_2O(O)C(CH_2)_2C(O)OCH_2C_6F_5$	17.42	0.28
		Phenols		
phenol	274	$C_6H_5OCH_2C_6F_5$	8.64	0.29
o-cresol	288	$CH_3C_6H_4OCH_2C_6F_5$	9.74	0.19
m-cresol	288	$CH_3C_6H_4OCH_2C_6F_5$	10.07	0.20
p-cresol	288	$CH_3C_6H_4OCH_2C_6F_5$	10.24	0.12
salicyaldehyde (2-hydroxybenzaldehyde)				
2-nitrophenol	319	$O_2NC_6H_4OCH_2C_6F_5$	15.40	0.59
3-nitrophenol	319	$O_2NC_6H_4OCH_2C_6F_5$	16.44	0.44
nitrocresol	333	$CH_3C_6H_3(NO_2)OCH_2C_6F_5$	16.06	0.32

[a] Molecular weight of derivatives. [b] Relative retention time (relative to PFBBr reagent peak). [c] Response factor relative to formic acid derivative. All responses were derived from the reconstructed 181 ion mass spectrum. [d] Not determined. [e] Diderivative.

chemical ionization (ECNICI) (*38*−*40*). The mass spectra of the PFBBr derivatives using these methods, however, show only specific *m/z* 181 ion and frequently do not provide adequate information for the determination of molecular weight or of compound structure.

In this study, we report for the first time the employment of pentafluorobenzyl alcohol (PFBOH) and methane as chemical ionization reagents to facilitate molecular weight determinations of PFBBr derivatives of carboxylic acids and phenols. We also demonstrate the power of the technique by identifying airborne carboxylic acids and phenols produced from the oxidation of isoprene and toluene in indoor and outdoor smog chamber experiments.

Experimental Section

Chemicals. PFBBr (also known as α-bromo-2,3,4,5,6-pentafluorotoluene), which is a strong lachrymator and should be handled with caution, was purchased from Aldrich Chemical Co., Inc., Milwaukee, WI. The reagents 18-crown-6 (18c6), tri-*n*-octylphosphine oxide (TOPO), and 2,3,4,5,6-pentafluorobenzyl alcohol (PFBOH) were also obtained from Aldrich. Potassium carbonate (K_2CO_3) and anhydrous sodium sulfate (Na_2SO_4) were of reagent grade and were used without further purification. All acids, phenols, and solvents were analytical or higher grade quality.

Preparation of Pentafluorobenzyl Esters and Ethers. The derivatization procedure used to prepare the pentafluorobenzyl esters and ethers was based on methods described by Brill *et al.* (*37*) and Glaceran *et al.* (*38*). Model compounds (Table 1) were chosen for their relevance to atmospheric systems and for structural variety.

A standard acid and phenol mixture (5 ng/mL each) in 1 mL of acetone was placed into a 3-mL screw-top vial and treated with 10 μL of 10% PFBBr in acetone, 50 μL of 18-crown-6 solution (4000 ng/mL in acetone), and about 10 mg of powdered potassium carbonate (K_2CO_3). The vial was stoppered and kept in a sonication bath at 40−60 °C for 2−3 h. Following completion of the reaction, the solution was filtered and a 1-μL injection was introduced for GC/MS analysis without further purification or cleanup.

TABLE 2. Relative Intensities of Characteristic EI Mass Spectra of PFBBr Derivatives of Carboxylic Acids and Phenols

		% realtive intensity (RI) of characteristic ions						
PFBBr ester of	M	*m/z* 197	*m/z* 181	*m/z* 161	M − 181	M − 197	M − 225	other
Monoalkanoic Acids								
formic acid	28	7	100	19	−[a]	NA[b]	NA	
acetic acid	14	5	100	13	7	99	NA	
propionic acid	11	2	100	9	−	51	NA	
butanoic acid	4	1	100	10	6	55	38	
valeric acid	1	1	100	11	31	39	31	41 (29)
hexanoic acid	2	2	100	11	17	27	15	69 (78), 43 (43)
Alkenoic Acids								
acrylic acid	15	3	66	10	−	100	NA	
methacrylic acid	29	2	86	13	−	100	57	221 (48)
vinylacetic acid	4	1	21	2	−	100	7	221 (55)
crotonic acid	5	−	9	2	−	100	2	221 (8)
Hydroxy Acid								
glycolic acid	2	4	100	13	3	6	NA	
Keto Acids								
pyruvic acid	−	−	80	4	−	−	100	
4-oxopentanoic acid	−	−	56	8	−	77	7	43 (100)
Aromatic Acids								
benzoic acid	27	1	46	9	−	100	49	51 (30)
hydroxyenzoic acid	13	−	100	8	5	6	−	
Diacids								
maleic acid	−	−	100	4	−	1	−	
succinic acid	−	6	100	13	−	15	5	101 (83)
Phenols								
phenol	70	−	100	13	5	4	−	65 (22)
o-cresol	53	−	100	10	18	3	−	77 (35)
m-cresol	54	−	100	9	5	3	−	77 (25)
n-cresol	74	−	100	11	41	3	−	77 (50)
salicylaldehyde	30	−	100	14	12	2	3	274 (25)
2-nitrophenol	7	−	100	8	−	−	−	
nitrocresol	6	−	100	8	−	−	−	137 (21)
3-nitrophenol	7	−	100	9	−	−	−	

[a] Not detectable or RI below 1%. [b] Outside selected mass range.

Sample Collection. Photochemical experiments were conducted either in an indoor 0.25-m^3 Teflon bag reactor (TBR) contained in an aluminum foil-lined box or in the UNC 150-m^3 Teflon outdoor dual smog chamber located near Pittsboro, NC.

Indoor TBR Experiment. Two types of TBR experiments were conducted: (1) organic compound mixed with NO_x/air and irradiated with UV radiation and (2) organic compound mixed with O_3/air in the dark. For first type of experiments, the TBR was exposed to constant irradiation from a mixture of black lamps and sun lamps at an intensity sufficient to photolyze NO_2 at a rate of about 4×10^{-4} molecule cm^{-3} s^{-1}. In a typical experiment, after the TBR was flushed and filled with clean air, about 10 ppmV of isoprene or toluene and 10 ppmV of nitrogen oxide (NO) were injected into the bag. Hydrogen peroxide (H_2O_2), which provides a source of OH radical by photolysis, was then delivered in the gas phase into the bag by bubbling clean air through an impinger containing 30% H_2O_2 solution. Once the initial condition had been established, the lights were turned on for up to 3 h. Midget impingers with glass joints were used for collection of the air samples. The impingers were wrapped in aluminum foil to avoid continued photochemical reaction of the acids during daylight sampling. Throughout the irradiation period, a single sample was taken for the duration of the experiment by pulling bag air into an impinger containing 10 mL of deionized water at a flow rate of about 0.5 L/min. The collected samples were transferred into amber bottles with Teflon-lined screw caps and stored in a refrigerator at 4 °C. Analysis followed within 24 h. In isoprene/ozone dark experiments, about 0.8 ppmV of ozone was initially added to the TBR, and then 10 ppmV of isoprene was injected. Air samples were collected in the same way as described above.

Outdoor Smog Chamber Experiments. The UNC chamber and its standard analytical instrumentations have previously been described (*41*). The chamber uses natural sunlight as its radiant energy source. For a typical daytime outdoor chamber run, 2 ppmV of the selected hydrocarbon (isoprene or toluene) and 0.67 ppmV of NO were injected into the chamber. Injections were made approximately 0.5 h before sunrise, and experiments typically ran until 1600 EDT. Air samples were collected from beneath the chamber floor with a Teflon sampling line no longer than 30 cm to minimize sample loss. A chamber background air sample was drawn 30 min prior to the hydrocarbon injections. Throughout the experiment, both batch and interval samples of 1 h were taken in the same way as those described for indoor experiments.

One isoprene/O_3 nighttime run was conducted on October 17, 1996, in which the initial conditions in the chamber were 4.8 ppmV of isoprene and ozone continuously injected at 0.3 ppm/h. Air samples were taken for intervals of 1 h throughout the 6-h experiment.

Sample Extraction and Preparation. After collecting chamber air samples in aqueous phase, carboxylic acids and/or phenols were extracted into the organic phase using a TOPO−methyl *tert*-butyl ether (MTBE) mixture solution. The use of TOPO for facilitating liquid extraction for organic compounds, *e.g.*, acetic acid, acrylic acid, and phenols, has been reported (*42*). Its low solubility in water and high electron-donating ability make TOPO a suitable extractant for polar molecules.

To monitor any losses of the organic acids and phenols in the entire analytical procedure, a known amount of hexanoic acid (10 μL, 400 ng/mL) was spiked into the collected aqueous sample prior to extraction. This acid was chosen

TABLE 3. Relative Intensities of Characteristic CH_4-CI Mass Spectra of PFBBr Derivatives of Carboxylic Acids and Phenols

PFBBr ester of	% relative intensity (RI) of characteristic ions									
	$M + 181$	$M + 29$	$M + 1$	M	$M - 1$	m/z 181	$M - 181$	$M - 197$	$M - 225$	m/z
Monoalkanoic Acids										
formic acid	–[a]	–	–	5	2	100	–	NA[b]	NA	
acetic acid	–	–	–	3	2	100	–	12	NA	
propionic acid	–	–	2	5	3	100	–	23	NA	434[c] (2)
butanoic acid	4	–	6	6	3	100	1	45	4	448[c] (3)
valeric acid	3	–	4	5	8	100	22	57	3	462[c] (3)
hexanoic acid	–	–	3	4	14	100	45	59	4	
Alkenoic Acids										
acrylic acid	1	–	2	10	1	100	–	15	–	
methacrylic acid	11	–	79	19	–	100	–	41	–	
vinylacetic acid	5	–	17	2	–	100	6	88	12	
crotonic acid	5	–	61	13	3	40	0	100	–	
Hydroxy Acid										
glycolic acid	–	–	1	2	–	100	–	2	–	
Keto Acids										
pyruvic acid	–	–	–	–	–	10	–	–	100	
4-oxopentanoic acid	–	–	7	1	–	12	–	100	–	
Aromatic Acids										
benzoic acid	–	–	36	11	–	100	–	42	–	
hydroxybenzoic acid	NA	–	19	1	–	100	3	57	1	
Diacids										
maleic acid	NA	–	15	1	–	100	–	2	–	
succinic acid	NA	–	16	1	–	100	–	29	–	
Phenols										
phenol	44	9	100	33	1	39	–	–	–	
o-cresol	15	13	100	35	12	22	13	–	–	
m-cresol	11	15	100	29	4	17	6	–	–	
p-cresol	10	15	100	41	10	21	10	–	–	
salicylaldehyde	49	24	100	30	47	40	19	–	–	275[d] (63)
2-nitrophenol	–	1	100	44	1	59	–	–	–	
nitrocresol	5	5	–	1	–	100	2	5	–	288[e] (84), 468[f] (26)
3-nitrophenol	1	3	100	3	–	23	–	–	–	274[e] (4)

[a] Not detectable or RI below 1%. [b] Outside selected mass range. [c] $M - H + 181$. [d] $MH - CO$. [e] $MH - NO_2$. [f] $M + 181 - NO_2$.

as an internal standard because it would not form in the atmospheric photochemical experiments and its PFBBr ester did not coelute with other acids and phenols. The collected aqueous samples were placed in 25-mL screw-capped culture test tubes and were extracted twice with 2 mL of 0.5% TOPO in MTBE after adding 2 drops of concentrated H_2SO_4. The combined MTBE extract was then dried over anhydrous sodium sulfate (Na_2SO_4) and evaporated with dry nitrogen gas to dryness. The resulting residue was redissolved in 1 mL of acetone containing 1 ng/mL of decafluorobiphenyl (DFBP) as the internal standard. The solution was then treated in a manner identical to that described for model compounds.

Instrumentation. *Spectrometric Analysis of the PFBBr Derivatives.* To demonstrate the detection ability and selectivity of this technique, a Varian Saturn II GC/ITMS was employed. The system used an on-column injection port and a RTX-5 60 m × 0.32 mm, 0.5 μm film thickness capillary column. The following conditions were used: injection temperature program, 60 °C for 0.2 min, 60−250 °C at 180 °C/min, 250 °C for the rest of time; column temperature program, 60 °C for 1 min, 60−290 °C at 8 °C/min, 290 °C for 10 min; injection volume, 1 μL. Sample analytes were analyzed in both EI and CI modes sequentially. The mass scan range was 40−650, and a scan time of 1 scan/s was chosen.

Introduction of PFBOH. The PFBOH was introduced directly into the ion trap cell using a two-hole graphite-vespel ferrule in the transfer line, while the methane was introduced through the CI inlet system to serve as both stabilization and reagent gas. The amount of PFBOH and CH_4 introduced into the trap was monitored by recording m/z 181^+ and 29^+ ions, respectively. A ratio of 1:1 for m/z 29^+ to m/z 181^+ of a CH_4-PFBOH gaseous mixture in the source of the mass spectrometer was employed in this study. The ion trap conditions under CH_4-PFBOH CI mode were setup as follows: automatic reaction control (ARC), 100 ms; CI maximum ionization time, 2000 ms; and CI maximum reaction time, 40 ms. The transfer line between the column and the ion trap was kept at 280 °C, and the manifold (ion source) was set at 175 °C. The reagent line and reagent flask, containing the PFBOH, were both kept between 60 and 70 °C.

Results and Disscussion

Electron-Impact Ionization (EI) Mass Spectral of PFBBr Derivatives of Carboxylic Acids and Phenols. The EI mass spectra of model compounds were evaluated to determine whether molecular weight information of PFBBr derivatives of unknown carboxylic acids and phenols could be obtained by interpreting the EI mass spectra. Table 2 summarizes the characteristic EI mass fragments of PFBBr derivatives of standard compounds. Of the acids and phenols examined for this study, the molecular ion (M^+) in EI mass spectra is present for most compounds except for the keto acids (pyruvic and 4-oxopentanoic acids), the diacids (maleic and succinic acids), and the nitrophenols. Although the molecular ions for phenolic compounds, *e.g.*, phenol, cresols, and salicylaldehyde, exhibit high relative intensities (RI = ~74%), most of the remaining compounds show intensities of less than 30%. The acid derivatives, primarily the alkanoic and alkenoic acids, show a strong ion with $m/z = M - 197$ resulting from a loss of $C_6F_5CH_2O$ from the derivative part of the analyte. This ion, however, is often at an m/z lower than 100, a region where many compounds exhibit fragment ions. Thus, to provide for identification of a previously

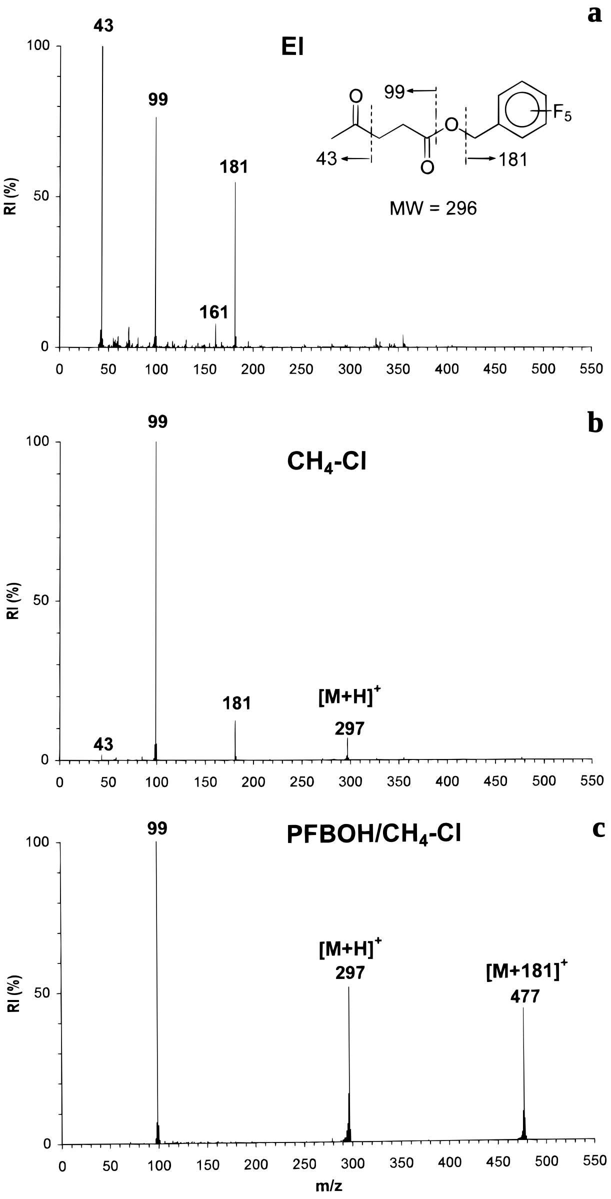


FIGURE 1. Comparison of ion trap mass spectra obtained by EI (a), CH_4-CI (b), and PFBOH/CH_4-CI (c) for the PFBBr derivative of 4-oxopentanoic acid. (Note: All mass spectra were background subtracted.)

unrecognized molecule, the mass spectra must exhibit either a high intensity molecular ion (RI > 30%) or a moderate intensity molecular ion (10−30%) along with a high $[M - 197]^+$ ion. In cases where either the molecular ion or the $[M - 197]^+$ ion is absent or in low abundance, it would be very difficult to identify carboxylic acids or phenolic compounds for which authentic standards do not exist.

In a manner similar to that for the pentafluorobenzyl derivatives of carbonyls (*33, 34*), the base peak in the EI mass spectra is mostly a fragment ion at *m/z* 181 ($C_6F_5CH_2^+$, pentafluorobenzonium ion). Although this ion is not very informative regarding structural elucidation or molecular weight determinations, it does provide an indication of the presence of a carboxyl or a phenoxy moiety in the original molecule. Our interpretation of the mass spectra also indicate that carboxylic acid derivatives may be distinguished from phenolic derivatives by the presence of an ion at *m/z* M − 225, due to the loss of $C_6F_5CH_2CO_2$.

Methane-Chemical Ionization (CH_4-CI) Mass Spectral Analyses. In previous research, Yu *et al.* (*34*) reported that a unique feature of the CH_4-CI mass spectra of PFBHA derivatives of carbonyl compounds is the appearance of an $[M + 181]^+$ ion. It is only observed in spectra obtained on an ion trap mass spectrometer due to the longer residence time of fragment ions as compared to beam instruments, and this promotes the secondary ion−molecule reactions. In their studies, the protonated $[M + H]^+$ ion was often the base peak in the CH_4-CI mass spectra, and the $[M + 181]^+$ ion was present at low relative abundance (RI < 10%). However, because the $[M + 181]^+$ ion was the highest mass and thus distinct from all other ions in the mass spectra, it was easy to recognize. Together, the presence of the $[M + H]^+$ and $[M + 181]^+$ ions served to confirm the molecular weight of the derivative unambiguously. To determine if $[M + H]^+$ and $[M + 181]^+$ ions also result with respect to PFBBr derivatives of carboxylic acids and phenols, CH_4-CI mass spectra of model compounds were examined, and the results are listed in Table 3.

As it can be seen, the $[M + H]^+$ ion is present as the base peak in the CH_4-CI mass spectra for most phenolic compounds; however, the RI of this ion for acid derivatives is considerably lower (<10%). As with the EI mass spectrum of tested acid derivatives, the CH_4-CI mass spectra are dominated by the *m/z* 181 ion. Sufficient energy is thus still imparted to the parent ion under CH_4-CI conditions to induce fragmentation of the molecules. It should be noted that an $[M + 181]^+$ ion is either absent or present at less than 11% RI for the alkanoic, the alkenoic, the hydroxy, and the keto acids. The phenols (phenol and cresols) meanwhile exhibit higher $[M + 181]^+$ relative ion intensities ranging from 10 to 49%. Again, as was the case with EI conditions, the abundance of $[M + 181]^+$, $[M + H]^+$, and $[M - H]^+$ ions for carboxylic acids are low, and the significance of these ions may be masked by background noise, making it difficult to identify PFBBr derivatives of carboxylic acids for which authentic standards are not available.

PFBOH Chemical Ionization Mass Spectral Analyses. Because the presence of an $[M + 181]^+$ ion in the mass spectra can assist in identifying the molecular mass of carboxylic acids, it was thought that a means to facilitate the identification and detection would be promotion of the formation of this ion by introducing a source of the pentafluorobenzyl cation (*m/z* 181^+) directly into the ion trap mass spectrometer. PFBOH was chosen as the precursor for the generation of pentafluorobenzyl cation because under CI conditions it gives the *m/z* 181 ion predominantly, comprising approximately 80% of the total ion current in the trap. In addition, the vapor pressure of PFBOH liquid is sufficient to allow its introduction in the gaseous phase to the mass spectrometer. In an effort to evaluate PFBOH as a CI reagent gas, a gaseous mixture of PFBOH and CH_4 was employed to examine the CI spectra of compounds, and the results from this work are summarized in Table 4. As noted, the PFBOH/CH_4-CI mass spectra of the examined compounds show increased RIs of both the $[M + 181]^+$ and $[M + H]^+$ ions for all acid derivatives except for glycolic and benzoic acids, which show no formation of $[M + 181]^+$ ion. While the $[M + 181]^+$ ion increases for all phenols and is the base peak for phenol, cresols, and salicylaldehyde, the RI of the $[M + H]^+$ ion decreases in the mass spectra, indicating that the formation of the $[M + 181]^+$ ion is favored for these compounds.

In light of our findings, we present the EI, CH_4-CI, and PFBOH/CH_4-CI ion trap mass spectra of 4-oxopentanoic acid in Figure 1 as a typical example. In this case, the predominant ions in the EI mass spectrum are at *m/z* 43 (M − 253), 99 (M − 197), and 181. The molecular ion (M^+) at *m/z* 296 is not evident, and thus it would be difficult to ascertain that the ion at *m/z* 99 is due to the loss of $C_6F_5CH_2O$ (*m/z* 197) from the parent derivative. Although the analysis of the molecular

TABLE 4. Relative Intensities of Characteristic PFBOH/CH_4-CI Mass Spectra of PFBBr Derivatives of Carboxylic Acids and Phenols

PFBBr ester of	% relative intensity (RI) of characteristic ions							other
	M + 181	M + 29	M + 1	M	M − 1	M − 181	M − 197	
Monoalkanoic Acids								
propionic acid	5	–[a]	10	43	34	–	100	434[c] (29)
butanoic acid	19	–	36	22	17	3	100	448[c] (32)
valeric acid	14	–	5	18	56	47	100	462[c] (36)
hexanoic acid	2	–	6	16	100	47	14	476[c] (6)
Alkenoic Acids								
acrylic acid	2	–	11	100	14	–	80	432[c] (16)
methacrylic acid	38	–	100	48	5	–	45	446[c] (6)
vinylacetic acid	23	–	73	17	4	–	100	401 (31), 221 (37)
crotonic acid	60	–	95	21	7	–	100	401 (39)
Hydroxy Acid								
glycolic acid	–	–	20	100	47	–	30	436[c] (6)
Keto Acid								
4-oxopentanoic acid	54	–	23	14	5	–	100	476 (11)
Aromatic Acids								
benzoic acid	–	–	100	46	14	–	85	
hydroxybenzoic acid	NA[b]	–	100	64	7	4	45	
Diacids								
maleic acid	NA	–	100	–	4	–	5	
succinic acid	NA	–	100	21	3	–	58	101 (74)
Phenols								
phenol	100	2	47	31	4	–	–	
o-cresol	100	3	49	39	13	6	–	
m-cresol	100	3	51	32	3	2	–	
p-cresol	100	4	55	47	13	5	–	
salicylaldehyde	100	10	81	61	79	9	–	455 (22), 275 (54)
2-nitrophenol	26	1	100	21	12	–	–	
nitrocresol	17	1	–	4	2	–	1	288[d] (29), 468[e] (100)
3-nitrophenol	32	2	100	14	4	–	–	454[e] (78)

[a] Not detectable or RI below 1%. [b] Outside selected mass range. [c] M − H + 181. [d] $MH - NO_2$. [e] $M + 181 - NO_2$.

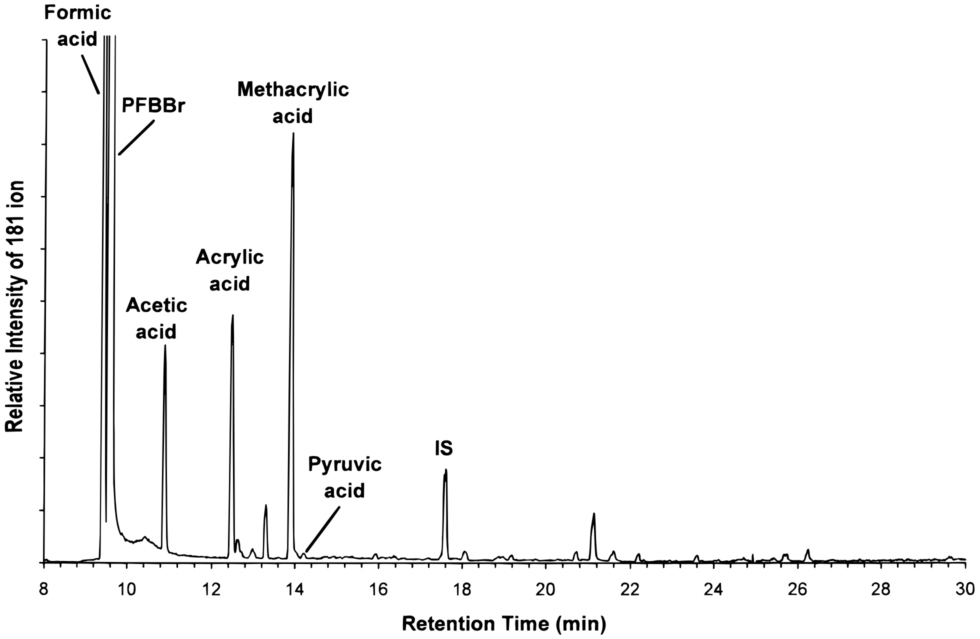


FIGURE 2. Reconstructed *m/z* 181 ion mass spectrum of a sample collected from an isoprene/O_3 outdoor nighttime experiment. (IS, hexanoic acid as an internal standard.)

weight of this analyte could be successfully conducted by interpreting the CH_4-CI mass spectrum, using PFBOH in combination with CH_4 as chemical ionization, the combination of an $[M + 181]^+$ ion (*m/z* 477) and a high abundance of protonated molecular ion (MH^+, *m/z* 297) makes it easy to determine the molecular weight of 4-oxopentanoate.

Carboxylic Acids Arising from the Oxidation of Isoprene. To further establish the value of utilizing PFBOH along with CH_4 as chemical ionization reagents to identify airborne carboxylic acids, we analyzed carboxylic acids resulting from hydroxyl radical oxidation of isoprene in TBR experiments and ozone oxidation in TBR and outdoor smog chamber experiments. The indoor isoprene/O_3 experiments showed the same carboxylic acid products as those in nighttime outdoor chamber experiments; therefore, only the results from the outdoor chamber experiments will be described.

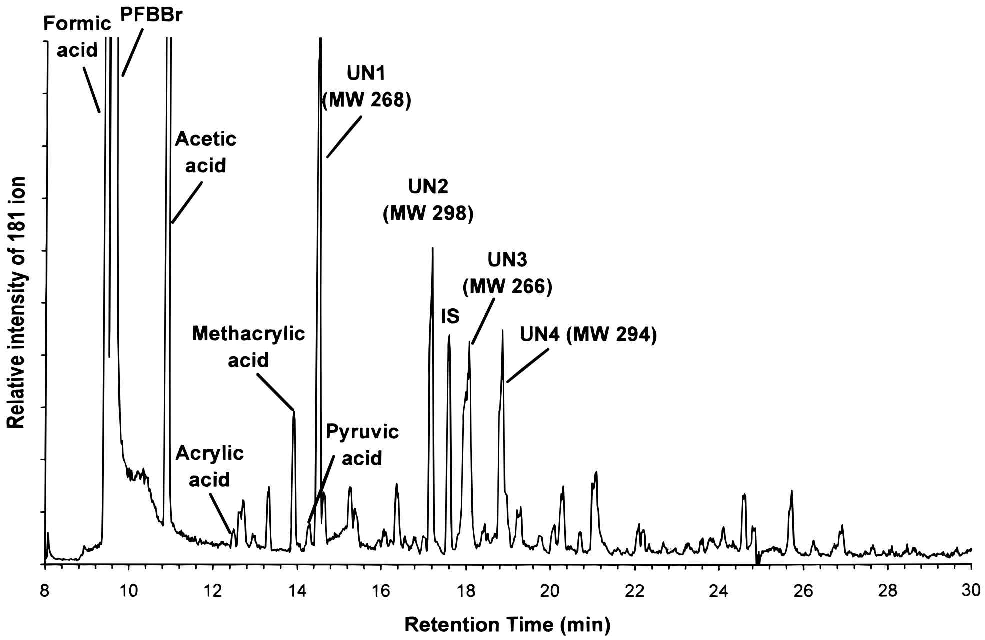
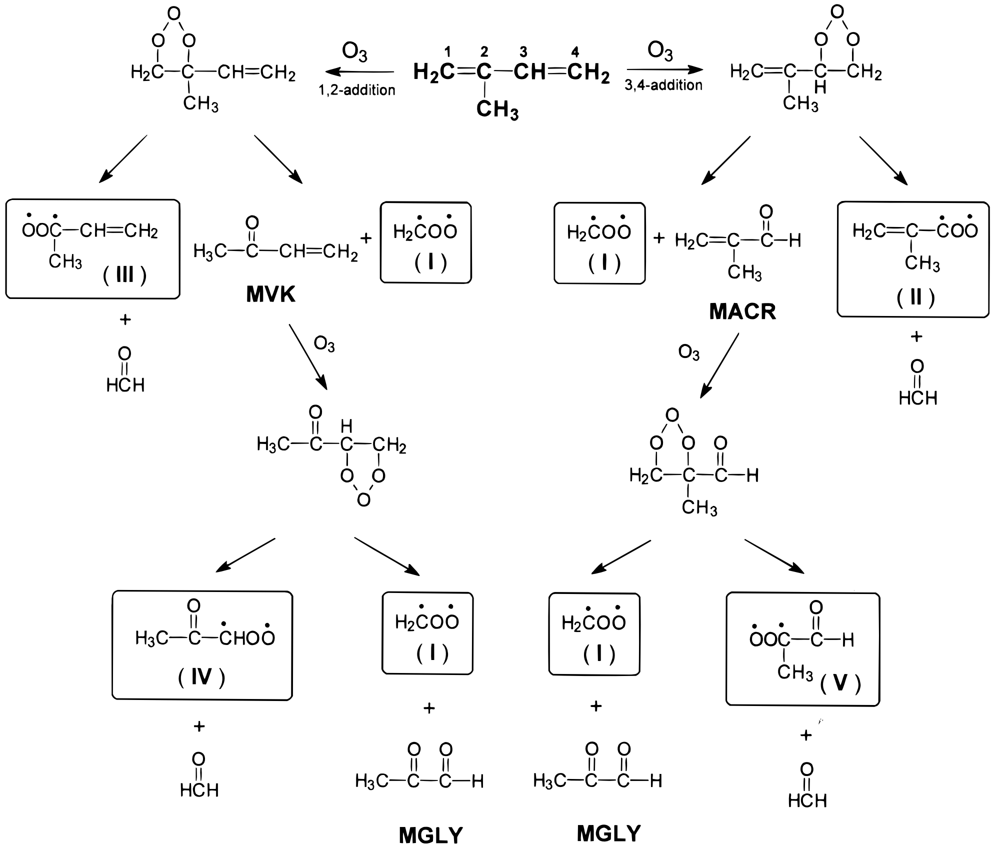


FIGURE 3. Reconstructed *m/z* 181 ion mass spectrum of a sample collected from an isoprene/NO_x TBR experiment. (IS, hexanoic acid as an internal standard.)

SCHEME 2. Formation of Possible Criegee Biradicals in Isoprene/O_3 Chemistry



The reconstructed m/z = 181 EI ion chromatograms of the sample extracts collected from these isoprene experiments are shown in Figures 2 and 3. By comparing the retention times and the resulting EI and CI-CH_4 mass spectra of the carboxylic acid products with those of the model compounds, we are able to identify formic, acetic, acrylic, pyruvic, and methacrylic acids in the samples.

While the production of formic and acetic acids has received extensive laboratory study (*6, 16, 43*), the formation of methacrylic acid had been only proposed by model prediction (*7, 44*), and we believe that its formation in this system has not previously been demonstrated experimentally. The production of acrylic acid has not previously been predicted as a product of isoprene in daytime or nighttime experiments. As indicated in Figures 2 and 3, we did detect it in our samples.

It has been known that the electrophilic addition of ozone to the unsaturated carbon−carbon bond of isoprene leads

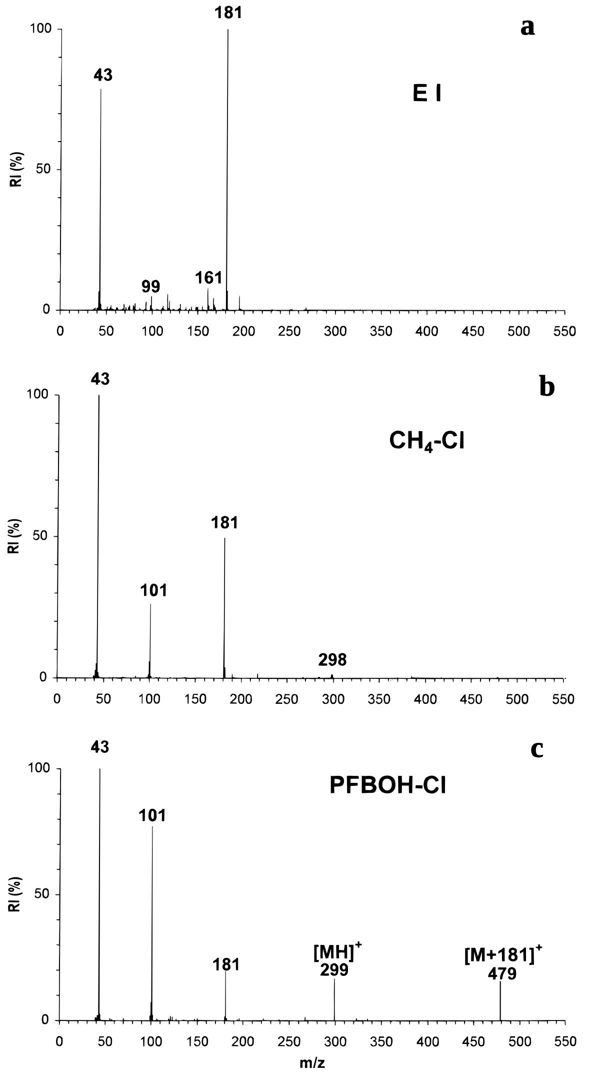
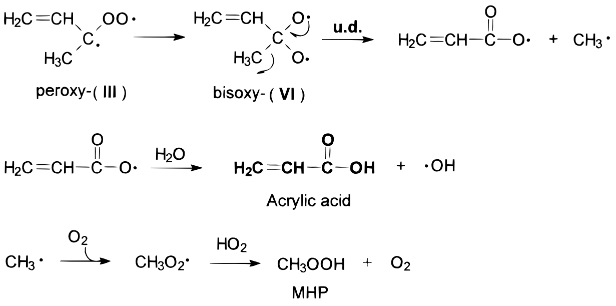
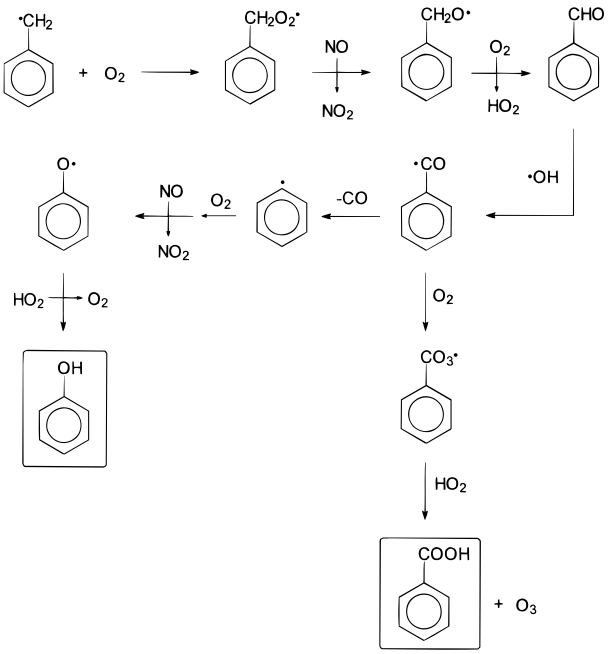


FIGURE 4. Mass spectra from EI (a), CH_4-CI (b), and PFBOH-CI (c) for PFBBr derivative of an unknown compound (UN2) from an isoprene/NO_x experiment.

SCHEME 3. Suggested Mechanism for the Formation of Acrylic Acid in Isoprene/O_3 Reactions



SCHEME 4. Possible Phenol and Benzoic Acid Formation Pathways



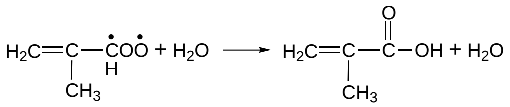
to the formation of several possible energy-rich Criegee biradicals (Scheme 2) (*45*, *46*). The unsubstituted biradical (**I**) either reacts with H_2O or is collisionally stabilized by the surrounding molecules to produce formic acid (HCOOH):

$$^{\bullet}CH_2OO^{\bullet} \xrightarrow{M} HCOOH + M \qquad (1)$$

$$\xrightarrow{H_2O} HCOOH + H_2O \qquad (2)$$

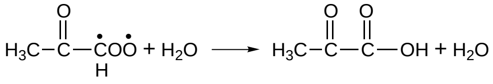
Reactions of the substituted biradicals (**II**−**V**) will form carbonyls such as methyl vinyl ketone (MVK) and methacrolein (MACR), dicarbonyls such as glyoxal and methyl glyoxal (MGLY), and hydroxycarbonyl products such as hydroxy acetone (*44*, *45*).

Jacob and Wofsy (*7*) have also proposed that biradicals **II** and **IV** should react primarily with H_2O in the same way as $^{\bullet}CH_2OO^{\bullet}$ to produce methacrylic acid and pyruvic acid:



$$H_2C{=}\underset{CH_3}{C}{-}\underset{H}{\dot{C}}O\dot{O} + H_2O \longrightarrow H_2C{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}{-}OH + H_2O \qquad (3)$$

(**II**) methacrylic acid



$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\dot{C}}O\dot{O} + H_2O \longrightarrow H_3C{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH + H_2O \qquad (4)$$

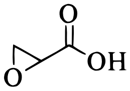
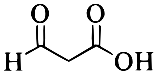
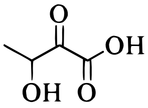
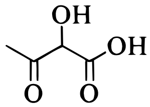
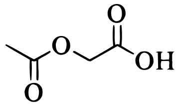
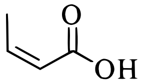
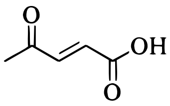
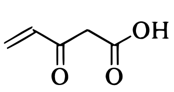
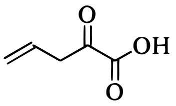
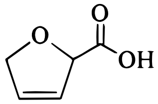
(**IV**) pyruvic acid

It has been suggested that the biradicals **III** and **V** would not react with water vapor to produce carboxylic acids, since the radical carbons of these biradicals are fully substituted (*47*), and instead would decompose to unreactive products (*9*, *44*). To explain the formation of acrylic acid in our experiments, a different mechanism is proposed as described below and diagrammed in Scheme 3.

The substituted peroxy biradical **III** can undergo rearrangement leading to a more stable bisoxy biradical **VI** (*48*, *49*), followed by a loss of the CH_3 radical via unimolecular decomposition and reaction with H_2O to yield acrylic acid (Scheme 3). The methyl hydroperoxide (MHP, CH_3OOH) formed from the reaction of the CH_3OO radical with the HO_2 radical has also been observed by Hatakeyama *et al.* (*50*) in the reaction of ozone with olefins having a methyl group.

It should be noticed that ozonolysis produces OH radicals (*51*, *52*) and that both OH and O_3 reactions occur in our experimental systems. The yield of acrylic acid in isoprene/NO_x TBR experiments (Figure 4), where OH radical reactions dominate, was very minor as compared to that in isoprene/O_3 reactions, suggesting that acrylic acid was formed predominately via isoprene/O_3 chemical pathways. In addition, the time series analysis in the isoprene/O_3 nighttime

TABLE 5. Proposed Structures of Unknown Carboxylic Acids from an Isoprene/NO_x TBR Experiment

Unknown	MW*	Formula	Possible Structures
UN1	268	$C_2H_3OCO_2H$	 
UN2	298	$C_3H_5O_2CO_2H$	  
UN3	266	$C_3H_5CO_2H$	 *cis*-Crotonic acid
UN4	294	$C_4H_5OCO_2H$	 (*cis*-, *trans*-)   

* Molecular weight of derivative

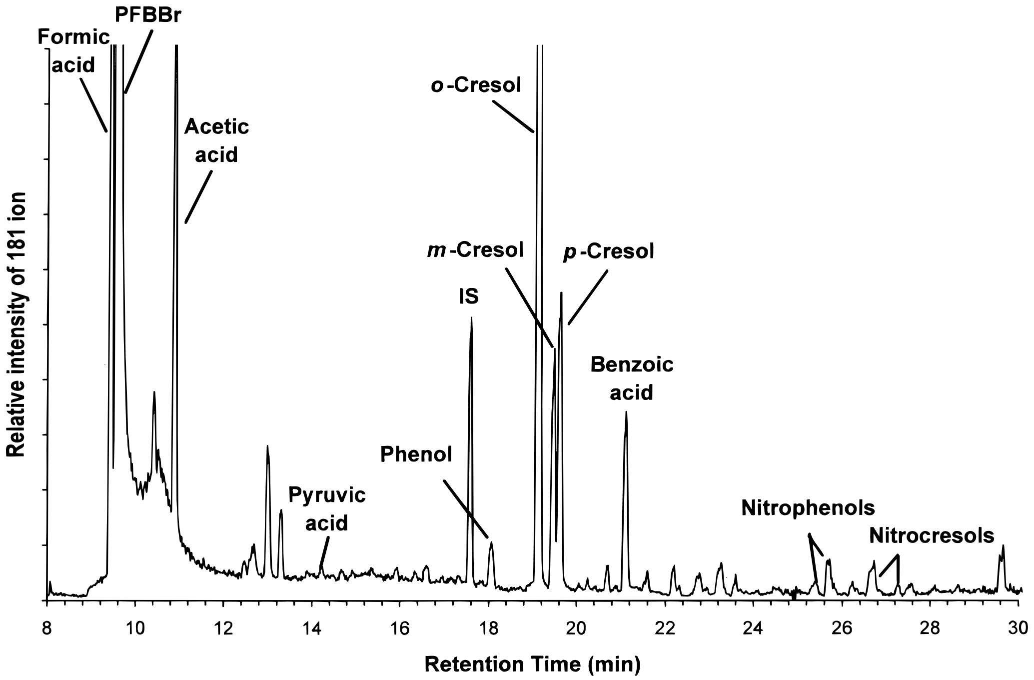
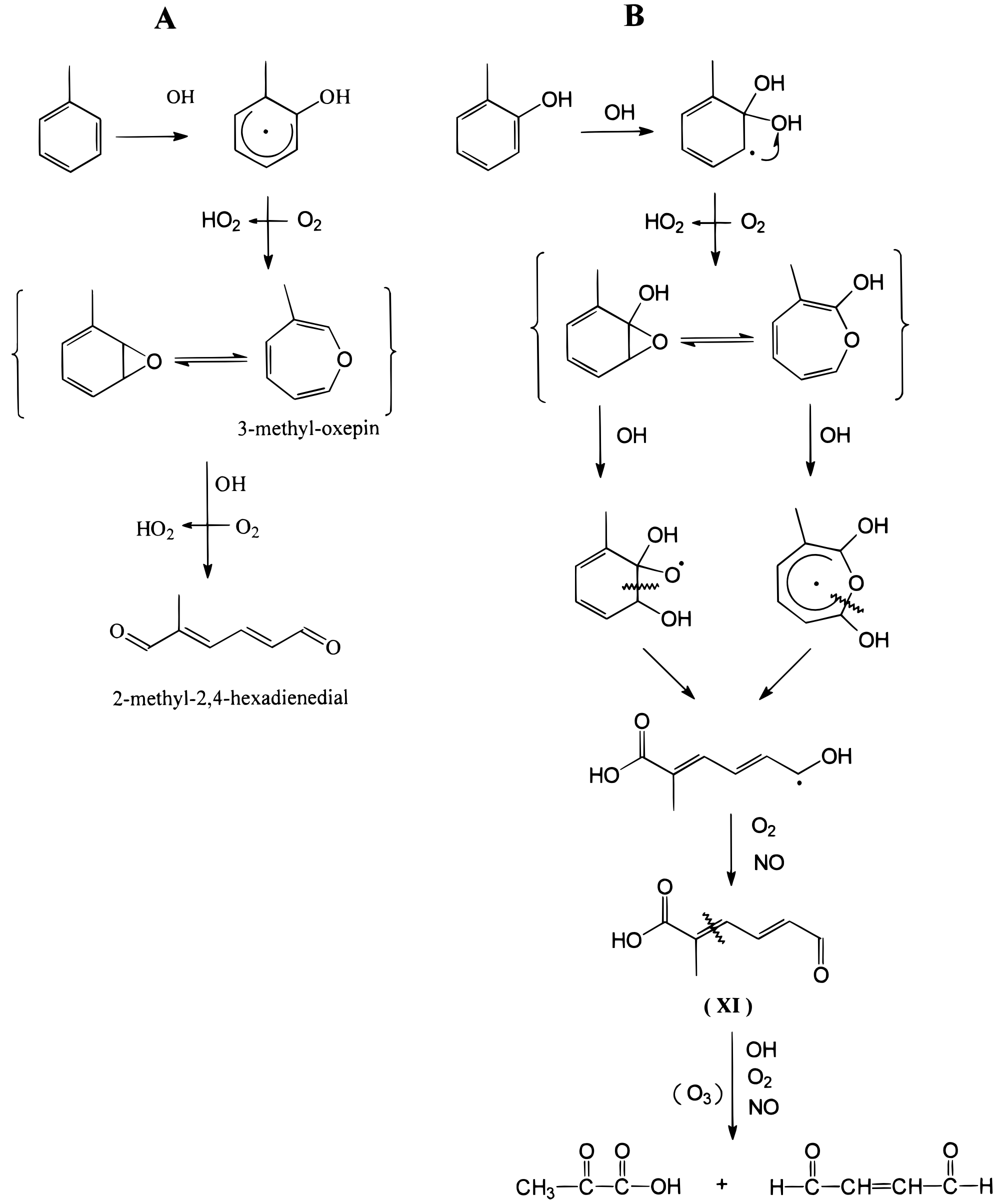


FIGURE 5. Reconstructed *m/z* 181 ion mass spectrum of a sample collected from a toluene/NO_x outdoor chamber experiment. (IS, hexanoic acid as an internal standard.)

outdoor chamber experiment showed that acrylic acid appeared immediately at the beginning of the experiment, and a linear increase in concentration as the reaction proceeded was observed as well. These observations also suggest that acrylic acid was formed as a direct product in isoprene/O_3 reaction.

For the unidentified compounds in Figure 3 whose molecular weights could not be clearly determined either from their EI or CH_4-CI mass spectra, the sample was subsequently analyzed using the new PFBOH/CH_4-CI method. The EI, CH_4-CI, and PFBOH/CH_4-CI mass spectra of the PFBBr derivative for an unknown compound (UN2) is shown in Figure 4 as an example of the power of this method. The absence or low intensity of the molecular ion in the EI and CH_4-CI makes it impossible to deduce the molecular weight of the derivative. In contrast, the presence of $[M + H]^+$ and $[M + 181]^+$ ions in the PFBOH/CH_4 mass spectra provides for easy determination of the molecular weight of the derivative, in this case 298, and for the formulation of possible structures of carboxylic acids consistent with this molecular weight. Possible structures consistent with MWs of other unknown acids are given in Table 5. Various unidentified carbonyl compounds including hydroxy carbonyls, unsaturated carbonyls, and epoxy carbonyls have been suggested in the oxidation of isoprene (*34*). Further oxidation of these compounds may lead to numerous carboxylic acids as

SCHEME 5. (A) Reaction Sequence Suggested by Yu et al. for Photooxidation of Toluene; (B) Possible Reaction Sequence Suggested in This Study for the Formation of Pyruvic Acid from OH-Initiated Oxidation of *o*-Cresol



suggested in Table 5. Because most authentic standards for the acids proposed in Table 5 are not commercially available, additional work is needed to verify their identities. In the case where further determination was possible, we propose that the compound with MW 266 is a C_4 unsaturated carboxylic acid. We have tentatively identified this as *cis*-crotonic acid after eliminating the other possible isomers—methacrylic, *trans*-crotonic, and vinylacetic acids—by comparing its retention time with authentic standards for these.

Carboxylic Acids and Phenols Arising from the Photooxidation of Toluene. A reconstructed ion chromatogram of a sample obtained from the photooxidation of toluene in the presence of NO_x in an outdoor smog chamber is given in Figure 5. We positively identified not only phenolic compounds (including phenol, cresols, nitrophenols, and nitrocresols) but also carboxylic acids (including formic, acetic, pyruvic, and benzoic acids).

Under atmospheric conditions, oxidation processes of toluene are mainly initiated by the reaction of OH radicals. Two major pathways are involved in the initial reactions: H-atom abstraction from the methyl group and OH radical addition to the aromatic ring (*53*). The phenolic compounds observed in our experiments result from the OH addition pathway, while benzoic acid is believed to arise from the H abstraction pathway. The formation of benzoic acid and phenol may arise from the continued reaction of benzaldehyde, a photooxidation product of toluene (*54*), with OH radical (Scheme 4).

Several recent studies have also suggested that the ring-opening products from the photooxidation of aromatics contain various carbonyl compounds (*54*–*56*). The reaction of O_3 with the unsaturated ring-opened intermediates can lead to numerous carboxylic acids. The reaction of OH with phenols can also yield keto acids, as suggested by Grosjean (*57*), where the OH-initiated photooxidation of *o*-cresol yields products including pyruvic acid. Since aromatic hydrocarbons comprise as much as 30% of the organics in urban atmospheric environments (*58*), they could be potential precursors of keto acids. A study by Yu *et al.* (*35, 36*) suggests a formation pathway leading to ring products, diunsaturated 1,6-dicarbonyls, for oxidation of toluene. The postulated mechanism in photooxidation of toluene involves the formation of 3-methyloxepin intermediate (Scheme 5A) similar to the benzene oxidation mechanism originally suggested by Barnes et al. (*59*, *60*). By analogy with their mechanism, the production of pyruvic acid from reaction of *o*-cresol with OH radicals can be explained by the reaction sequence depicted in Scheme 5B. Full evaluation of this mechanism, however, awaits positive identification of the production of the OH-substituted benzene oxide/oxepin intermediate and the diunsaturated oxo acids (**XI**).

In this work, we have demonstrated an advanced technique for analyzing airborne carboxylic acids and phenols from various chamber experiments as their PFBBr derivatives by using GC-ion trap mass spectrometry with the CI reagent-PFBOH. The resulting CH_4-PFBOH CIMS can be characterized by the appearance of the $[M + 181]^+$ ions, facilitating molecular mass determination of carboxylic acids. More detailed mass spectrometry aspects are currently under investigation and will be reported in a future paper.

Acknowledgments

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