International Journal of Mass Spectrometry 190/191 (1999) 343–357

The power of pentafluorobenzyl alcohol chemical ionization/ion trap mass spectrometry to identify pentafluorobenzyl derivatives of oxygenated polar organics

Paul Frazey[a], Xin Rao[b], Reggie Spaulding[b], Brian Beld[b], M. Judith Charles[b,*]

[a] *Department of Chemistry, Plattsburgh State University of New York, Plattsburgh, NY 12901, USA*
[b] *Department of Environmental Toxicology, University of California, Davis, Davis, CA 95616, USA*

Received 30 September 1998; accepted 26 January 1999

Abstract

Chamber studies establish that oxygenated and polar organics such as carbonyls, dicarbonyls, hydroxy carbonyls, epoxy carbonyls, oxo acids, and hydroxy carboxylic acids are photooxidation products of biogenic and anthropogenic hydrocarbons. To date, with the exception of carbonyls and carboxylic acids, few studies report ambient measurements of oxygenated and polar organics because of a lack of suitable methodologies. Such measurements are critical to establish the accuracy of photochemical models that incorporate chamber data, and are formulated to devise strategies to improve air quality. Here, we demonstrate the power and utility of pentafluorobenzyl alcohol (PFBOH) to identify pentafluorobenzyl derivatives of oxygenated and polar organics. The PFBOH chemical ionization (CI) mass spectrum comprises three primary ions at *m/z* 181 $(C_6F_5CH_2)^+$, 197 $(C_6F_5CH_2O)^+$, and 198 $(C_6F_5CH_2OH)^{+\cdot}$. We report the presence of $(M - H)^+$, $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$ ions in the PFBOH mass spectra that create a unique pattern which facilitates molecular weight determinations. By conducting experiments in which the reagent ions were selected prior to reaction with the derivative molecules, we established that the *m/z* 181 reagent ion effects the formation of an $(M + 181)^+$ adduct ion. The data also suggest that the *m/z* 197 ion primarily affects proton addition reactions, and that the *m/z* 198 ion promotes charge exchange and hydride abstraction reactions. We establish the practicality and power of PFBOH to identify pentafluorobenzyl derivatives in this and previous work. The knowledge gained regarding ion/molecule reactions of PFBOH chemical ionization (CI) was utilized to identify a pentafluorobenzyl derivative in an extract of fine particulate matter of diesel motor vehicle exhaust in a traffic tunnel. The combination of pentafluorobenzyl derivatization, PFBOH, and ion trap mass spectrometry assisted the identification of 4-hydroxybenzoic acid as a component of the particulate organic matter. (Int J Mass Spectrom 190/191 (1999) 343–357) © 1999 Elsevier Science B.V.

Keywords: Pentafluorobenzyl alcohol; Pentafluorobenzyl derivatives; Oxygenated and polar organics; Chemical ionization/ion trap mass spectrometry

1. Introduction

Widespread attention is being paid to characterizing the molecular composition of fine particulate matter because of the association of this material with respiratory and cardiovascular illnesses, and the critical role that such matter plays in haze formation. Secondary organic aerosols that constitute as much as 80% of the organic carbon in smog [1] are produced from the photooxidation of hydrocarbon emissions and subsequent gas/particle partitioning of the prod-

---

* Corresponding author. E-mail: mjcharles@ucdavis.edu

Dedicated to J.F.J. Todd and R.E. March in recognition of their original contributions to quadrupole ion trap mass spectrometry.

PII S1387-3806(99)00026-3

ucts [2,3]. The hygroscopicity of the organics and the particulate mass affect the partitioning process [2,4]. Molecular characterization of organic particulate matter is also necessary to gain insight into processes that govern their formation. To date, only 15–60% of the organics in particulates have been measured by collecting particles on filters, extracting the organics with solvent, and employing gas chromatography/mass spectrometry (GC/MS) for detection [3,5,6]. These methods preferentially measure nonpolar molecules, and thus the unidentified fraction is proposed to comprise oxygenated and polar molecules that require derivatization to be detected by GC/MS methods [6,7,8].

Pentafluorobenzyl derivatization/ion trap mass spectrometry methods have already played a critical role in the identification of gas phase photooxidation products that may partition to particulate matter. Yu et al. [9,10] were the first to apply *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) derivatization along with ion trap mass spectrometry to identify products in chamber studies. The power of the method is due to selectivity of the reagent for carbonyl moieties and the presence of ions that facilitate molecular weight determinations. Such ions are not observed in the PFBHA mass spectra on beam instruments [11]. They are only observed in an ion trap, and include those resulting from typical chemical ionization reactions (e.g. proton transfer and charge exchange), as well as an $(M + 181)^+$ ion, assumed to arise from the reaction of the *m/z* 181 $(C_6F_5CH_2)^+$ pentafluorobenzyl fragment ion of the derivative and neutral analyte molecules. By observing the juxtaposition between this unique ion and the $(M + H)^+$ ion, as well as other common ions, Yu et al. [9,10] identified novel carbonyl, dicarbonyl, oxo acid, hydroxy carbonyl, and epoxy carbonyl photooxidation products of isoprene (a biogenic hydrocarbon emission) and alkyl benzenes (compounds present in anthropogenic emissions). Because the generation of the $(M + 181)^+$ ion is dependent on the concentration of the pentafluorobenzyl cation, we explored pentafluorobenzyl alcohol ($C_6F_5CH_2OH$; PFBOH) as a chemical ionization reagent to effect the formation of $(M + 181)^+$ ions. By using methane along with PFBOH, we identified unknown pentafluorobenzyl derivatives (PFB) of novel carboxylic acids and phenolic products from the photooxidation of isoprene and toluene, a model for anthropogenic emissions in chambers [12]. The significance of that study was its contribution to the understanding of atmospheric photooxidation reactions, the introduction of a novel chemical ionization reagent to identify pentafluorobenzyl derivatives, and the demonstration that utilization of pentafluorobenzyl derivatization reagents along with ion trap mass spectrometry affords molecular weight determinations for compounds that could not be identified by using other methods.

Both our study and that of Yu et al. [9,12] improved the identification and detection of hydroxy carbonyls and oxo acids by silylating the hydroxy and carboxy functionalities on PFBHA derivatives with *bis* (trimethyl silyl) trifluoroacetamide (BSTFA). Yu et al. [9] identified unique products arising from the oxidation of the biogenic hydrocarbons α-pinene and Δ^3 carene. We identified hydroxy carbonyls and oxo acids in air by using PFBHA/BSTFA derivatization and PFBOH chemical ionization/ion trap mass spectrometry. We also established that PFBOH effects the formation of molecular and *pseudo* molecular ions for PFBHA derivatives of methyl vinyl ketone, methacrolein, methyl glyoxal, and hydroxy acetone. The significance of this work was that it was the first field measurement of carbonyls utilizing pentafluorobenzyl derivatization along with ion trap mass spectrometry, and it was the first measurement of hydroxy acetone and 3-hydroxy butanone in the ambient atmospheric environment.

Here, we add to the body of knowledge about ion trap mass spectra of PFBHA, PFBHA/BSTFA, and PFBBr derivatives by comparing the ability of electron ionization (EI), methane chemical ionization (CI), and PFBOH CI to yield molecular and *pseudo* molecular ions to facilitate molecular weight determinations. We also explore the reactions of the PFBOH reagent ions by conducting mass-selected chemical ionization experiments, and we demonstrate that the knowledge gained can be put to practical use to identify an unknown compound in a particulate matter sample extract.

2. Experimental

2.1. Chemicals

We employed *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) to derivatize the carbonyls, *bis* (trimethylsilyl) trifluoroacetamide (BSTFA), and N *tert*-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) as silylation reagents, and pentafluorobenzyl bromide (PFBBr) to derivatize carboxylic acids. Derivatization reagents as well as pentafluorobenzyl alcohol, 18-crown-6, powdered potassium carbonate, and authentic standards were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI.

2.2. Sample collection and preparation

We sampled fine particulate matter ($PM_{2.5}$) from the Caldecott Tunnel (Walnut Creek, CA) on November 17–20, 1997. We present a mass spectrum obtained from a sample extract of the heavy-duty (diesel) vehicle bore of the tunnel from 3:15 p.m. on November 17 to 12:00 p.m. on November 18, 1997. Fine particulate matter was collected using a single Interagency Monitoring of Protected Visual Environments (IMPROVE) Module Aerosol Sampler. Particles larger than 2.5 μm in diameter were removed by a cyclone separator operating at 22.8 L/min. We utilized two samplers in parallel. One sampler was equipped with 2-μm pore size teflon filters so that we could determine the total aerosol mass by the difference in weight of the filters before and after sampling. The other sampler was equipped with quartz fiber filters. Filters were sonicated in acetone at -8 °C for 2 min, and the extract was derivatized with pentafluorobenzyl bromide according to a methodology similar to Chien et al. [12].

2.3. Gas chromatography/ion trap mass spectrometry

We utilized a Varian Star 3400 CX gas chromatograph/Varian Saturn 2000 ion trap mass spectrometer (GC/ITMS; Varian, Walnut Creek, CA) with a RTX-5MS chromatographic column (0.32 mm inner diameter (i.d.) and 0.25 μm film thickness; Restek Corp., Bellefonte, PA). The linear velocity of the helium carrier gas was 30 cm/s. The injector temperature was increased from 280 °C to 320 °C at 180 °C/min. The GC oven was initially held at 69 °C for 1 min, then ramped to 100 °C at 5 °C/min, and then to 320 °C at 10 °C/min, and held for 4 min at 320 °C. The transfer line and manifold temperatures were 270 °C and 40 °C, respectively. We utilized a trap temperature of 150 °C in the chemical ionization experiments, and a trap temperature of 200 °C in the electron-impact ionization experiments. The axial modulation voltage was 4.0 V and the emission current was 10 μamps in all the experiments. We used the instrument auto-tune program to optimize the automatic gain control target (AGC) and multiplier voltage.

2.4. Electron-impact ionization (EI)

The EI mass spectra were obtained using the automatic gain control (AGC) software to adjust the ionization time to optimally fill the trap with ions. The AGC prescan ionization time was 100 μs and the prescan storage level was *m/z* 45. The maximum ionization time was set to 25 000 μs. EI spectra were acquired over a mass range of 45–650 amu.

2.5. Methane chemical ionization (methane CI)

We conducted the methane chemical ionization in the selected ejection chemical ionization mode (SECI). In this mode, a waveform is used to eject ions generated by EI prior to the period methane ions react with analyte molecules. Ions greater than the *m/z* of the reagent ions were then ejected by utilizing a reagent ion ejection amplitude of 9 V. A storage level of *m/z* 5 and a reaction storage level of *m/z* 13 were employed. Automatic gain control was used to adjust the ionization time and reaction time in order to fill the trap with ions. The maximum ionization time and maximum reaction time were set to 2000 μs and 40 ms, respectively. The methane CI mass spectra were acquired over a mass range of 50–650 u.

2.6. PFBOH chemical ionization

We introduced PFBOH into the ion trap in a method similar to that of Chien et al. Approximately

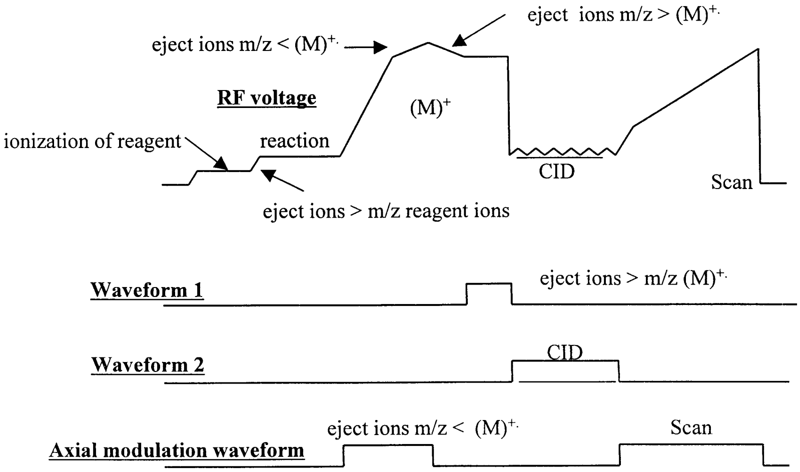


Fig. 1. Scan function for selection of PFBOH reagent ions prior to reaction with neutral analyte molecules.

5 mL of PFBOH was added to a 10 mL round-bottom flask fitted with a ¼ in. outer diameter (o.d.) neck. The flask was attached to a 20-in. length of stainless steel tubing (⅛ in. o.d.) with a graphitized-vespel ferrule and a stainless steel reducing union. The stainless steel tubing was connected to a 50-cm length of fused silica capillary tubing (0.32 mm i.d.) inside the GC oven with a graphitized-vespel ferrule and reducing union. The transfer line ferrule was replaced by a two-hole ferrule so that the fused silica tubing could be introduced to the ion trap in parallel with the chromatography column. The SECI waveform was disabled by setting the reagent ion ejection amplitude to 0. We employed an ionization storage level and reaction storage level of *m/z* 25. The background mass of 230 was sufficient to eject residual reagent ions from the trap prior to mass detection. In the analysis of standards, the spectra were obtained under fixed ionization and reaction times of 100 μs and 128 ms, respectively. In the analysis of field samples, ARC was used with maximum ionization and reaction times of 300 μs and 128 ms, respectively.

We conducted mass-selected reagent ion CI experiments to explore ion/molecule reactions between the PFBOH reagent ions and derivative molecules. In these experiments, we modified the tandem mass spectral scan function according to the scan function presented in Fig. 1. The scan function comprises six steps: (1) ionization of the reagent ions, (2) isolation of reagent ions, (3) reaction of reagent ions with neutral analyte molecules, (4) isolation of molecular or *pseudo* molecular ions, (5) collisional induced dissociation (CID), and (6) detection of the ions. In the typical tandem mass spectral scan function, CID is performed by applying a supplemental dipole field to the endcap electrodes (waveform; WF-2) after step four. In our experiment, the CID amplitude was zero to inhibit any CID reactions. We observed optimal results by using a reaction time of 128 ms and the CID time to 100 ms. An ionization and reaction storage level of *m/z* 25 was employed. The ionization time was varied between 100 and 300 μs to create reagent ion intensities similar to those observed in experiments in which the reagent ions were not isolated. Isolation of the reagent ions was accomplished by utilizing an excitation storage level of *m/z* 86, to isolate the *m/z* 198 and 197 ions, and *m/z* 78 to isolate the *m/z* 181.

3. Results and discussion

3.1. Comparison of EI, methane CI, and PFBOH CI mass spectra for identification of pentafluorobenzyl derivatives

The EI and methane CI mass spectra of PFBHA derivatives of aldehydes, ketones, hydroxy carbonyls, and dicarbonyls [9,11,13]; the EI, methane CI, and the

Table 1
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBHA derivatives of aldehydes and ketones

Compound (molecular weight of the derivative)	Retention time (relative retention time)	Mode of ionization	Ion (% relative intensity)[a]				
			$(M-H)^+$	$(M)^+$	$(M+H)^+$	$(M+181)^+$	*m/z* 181
Acetaldehyde (239)	9.31 (0.509)	EI					100
	9.29 (0.508)	Methane CI		5	100; **100**	4; 7	36
	9.29 (0.508)	PFBOH CI	13	52	84	100	[b]
Acetone (253)	10.48 (0.572)	EI		7			
	10.44 (0.577)	Methane CI			100; **100**	–; **2**	4
	10.41 (0.571)	PFBOH CI	15	100	84	94	[b]
Propionaldehyde (253)	10.86 (0.593)	EI					100
	10.84 (0.592)	Methane CI			100	2	18
	10.84 (0.593)	PFBOH CI		11	77	100	[b]
2-Butanone (267)	11.98 (0.654)	EI					100
	11.98 (0.654)	Methane CI			100		
	11.98 (0.655)	PFBOH CI	7	19	91	81	
Methacrolein (265)	12.19 (0.666)	EI		15		1	
	12.18 (0.665)	Methane CI		5	100; **100**	–; **4**	
	12.18 (0.666)	PFBOH CI	22	100	56	64	[b]
Methyl vinyl ketone (265)	12.34 (0.674)	EI	6.0	27			100
	12.34 (0.674)	Methane CI	7	7	100; **100**	–; **9**	
	12.33 (0.674)	PFBOH CI	60	100	51	49	[b]
4-Fluorobenzaldehyde (319)	18.21 (1.000)	EI	27	45	15		100
	18.21 (1.000)	Methane CI		2	36		
	18.21 (1.000)	PFBOH CI	22	100	57	39	0
o-Tolualdehyde (315)	19.54 (1.067)	EI	27	45	15		100
	19.53 (1.067)	Methane CI		2	36		
	19.53 (1.068)	PFBOH CI	22	100	57	39	[b]

[a] Blanks and dashes indicate that ions were absent or <1% relative intensity.
[b] Mass range detected was *m/z* 230 to *m/z* 650. Thus, ions not detected in PFBOH CI mass spectra.
Boldface values are reported by Yu et al. [9].

methane/PFBOH CI mass spectra of PFBBr derivatives of carboxylic acids and phenols [12]; and the EI and methane CI mass spectra of PFBHA/BSTFA derivatives of mono- and di-carboxylic acids, hydroxy carbonyls, and oxo acids [14] were characterized in previous research. Here, we present the first data on utilizing PFBOH as a chemical ionization reagent by itself, and we focus on that ability of EI, methane CI, and PFBOH CI to yield ions that provide structural or molecular weight information.

We present data on the percent relative intensities for model pentafluorobenzyl derivatives of aldehydes, ketones, dicarbonyls, hydroxy carbonyls, oxo acids, hydroxy acids, mono- and di-carboxylic acids, and alkenoic acids in Tables 1–6. For many of the PFBHA and PFBHA/BSTFA derivatives, two oxime isomers are generated. In such cases, we present the data for the more abundant isomer. In cases in which the heights of the chromatographic peaks are similar, we arbitrarily chose the data for one of these peaks. We also compare the percent relative intensities reported here with those reported in other work. For comparative purposes, these data are presented in the tables as bolded values. As evident from the tables, we also report the percent relative intensities of compounds for which no previous data exists. Thus, our data complement and augment previous work. Most important, we discuss the PFBOH CI ion trap mass spectra for pentafluorobenzyl derivatives of aldehydes, ketones, dicarbonyls, and the PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids for which no previous data exists.

3.2. PFBHA derivatives of aldehydes, ketones, and dicarbonyls

The EI mass spectra of the model compounds, with the exception of the aromatic aldehydes, *o*-tolualde-

Table 2
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBHA derivatives of dicarbonyls

Compound (molecular weight of derivative)	Retention time (relative retention time)	Mode of ionization	Ion (% relative intensity)[a]				
			$(M - H)^+$	$(M)^+$	$(M + H)^+$	$(M + 181)^+$	*m/z* 181
2,3-Butanedione (476)	21.99 (1.201)	EI		2			100
	21.99 (1.201)	Methane CI	–; **9**	–; **83**	9	[b]	18; **46**
	21.99 (1.208)	PFBOH CI		47	100	[b]	[c]
Glyoxal (448)	21.10 (1.153)	EI		16			100
	21.23 (1.159)	Methane CI		–; **4**	16; **100**	3; **17**	100
	21.11 (1.159)	PFBOH CI	11	100	76	15	[c]
Methyl glyoxal (448)	21.61 (1.180)	EI		4			100
	21.61 (1.180)	Methane CI			39; **88**	2; **39**	100; **100**
	21.61 (1.182)	PFBOH CI	11	38	100	20	[c]
2,4-Pentanedione (490)	22.46 (1.227)	EI				[b]	100
	22.46 (1.227)	Methane CI			11; **57**	[b]	10; **100**
	22.46 (1.228)	PFBOH CI			43	[b]	[c]

[a] Blanks and dashes indicate that ions were absent or <1% relative intensity.
[b] Mass range detected was *m/z* 230 to *m/z* 650. Thus, ions were not detected in PFBOH CI mass spectra.
[c] The *m/z* of the $(M + 181)^+$ ion is greater than the mass range of the instrument, and thus could not be detected.
Boldface values were reported by Yu et al. [9].

hyde and fluorobenzaldehyde, are characterized by an *m/z* 181 pentafluorobenzyl fragment ion $(C_6F_5CH_2)^+$ as the base peak, and if present, $(M)^{+\cdot}$ and $(M + 181)^+$ ions that exhibit low relative intensities. Thus, it is difficult to determine the molecular weight of a compound by examining such mass spectra. The presence of the *m/z* 181 ion, however, is an excellent indicator that carbonyls are present [9,11–14].

Hydride ion abstraction, charge exchange, and proton transfer reactions can produce $(M - H)^+$, $(M)^{+\cdot}$, and $(M + H)^+$ ions, respectively, under methane CI conditions. For the aldehydes and ketones, the $(M + H)^+$ ion is generally the base peak, indicating that proton addition reactions are favored for these compounds. These data are in good agreement with the data reported by Yu et al. [9] presented as bolded values in the table. For the PFBHA derivatives of 2,3-butanedione, glyoxal, and methyl glyoxal, either the $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$ were absent or <1%, or lower than the values reported by Yu et al. [9]. Most notably, significant differences were observed in the intensity of the $(M + H)^+$ ion. Because the concentrations of the derivatives are similar (1 ng/μL), we postulate that these differences are due to methane pressure despite the appearance of similar operating conditions. Enhancement of the $(M - H)^+$, $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$ was accomplished when PFBOH was utilized as the chemical ionization reagent instead of methane. For the PFBHA derivatives of aldehydes and ketones, significant differences were observed in the formation of the $(M + 181)^+$ ions. In most cases PFBOH also effected charge exchange and hydride abstraction reactions that were not apparent when methane was utilized as the reagent.

3.3. PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids

Silylation of the hydroxyl group on PFBHA derivatives of hydroxy carbonyls and oxo acids affords greater sensitivity due to drastic improvements in the chromatography [15]. For oxo acids such as pyruvic acid, the combination of these reagents also affects the production of molecular and *pseudo* molecular ions in the methane and PFBOH CI mass spectra that are not as apparent in the mass spectra of the pentafluorobenzyl bromide derivatives of these acids.

The EI mass spectra of PFBHA/BSTFA derivatives are characterized by $(M - CH_3)^+$, *m/z* 181, *m/z* 73, and *m/z* 75 ions. The *m/z* 73 $(CH_3)_3Si^+$ and *m/z* 75 $HO{=}Si(CH_3)_2^+$ ions arise from fragmentation of the

Table 3
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBHA/BSTFA derivatives of hydroxy carbonyls

Compound (molecular weight of derivative)	Retention time (relative retention time)	Mode of ionization	Ion (% relative intensity)[a]								
			$(M-H)^+$	$(M)^+$	$(M+H)^+$	$(M+181)^+$	$(M-15)^+$	$(M-89)^+$	*m/z* 181	*m/z* 75	*m/z* 73
3-Hydroxy-2-Butanone (355)	15.31 (0.834)	EI					99		72	32	88
	15.23 (0.833)	Methane CI	3	12	17		63	100			
	15.24 (0.832)	PFBOH CI	6	10	39	59	78	100	[b]	[b]	[b]
Hydroxyacetone (341)	15.46 (0.842)	EI		–; **25**			100; **100**		67; **57**	24; **17**	70; **62**
	15.38 (0.841)	Methane CI	5	8	93; **100**	–; **17**	94; **99**	100	7		0
	15.39 (0.841)	PFBOH CI	8	11	63	62	100	64	[b]	[b]	[b]
1-Hydroxy-2-Butanone (355)	16.24 (0.885)	EI					100		88	37	96
	16.16 (0.884)	Methane CI	8	8	94		76	100	6		
	16.18 (0.884)	PFBOH CI		21	77	73	100	85	[b]	[b]	[b]
5-Hydroxy-2-Pentanone (269)	18.05 (0.983)	EI						8	100	26	58
	17.96 (0.982)	Methane CI	4	3	11			100	0		
	17.98 (0.982)	PFBOH CI	8	7	36	23			[b]	[b]	[b]
1,3-Dihydroxyacetone (429)	18.58 (1.012)	EI					36	14	59	12	100
	18.49 (1.011)	Methane CI	4	5	16	2	35		11		
	18.51 (1.011)	PFBOH CI	10	12	30	24	43	25	[b]	[b]	0
4-Hydroxybenzaldehyde (389)	22.53 (1.237)	EI		100	23				35	8	46
	22.44 (1.227)	Methane CI		15	100		6				
	22.46 (1.227)	PFBOH CI		100	50	26			[b]	[b]	[b]
2,3-Dihydroxy-benzaldehyde (477)	23.78 (1.295)	EI		5	2	[c]	100		11		24
	23.68 (1.295)	Methane CI		72	70	[c]	29				11
	23.69 (1.294)	PFBOH CI		72	71	[c]	100		[b]	[b]	[b]
2,3,4-Trihydroxy-benzaldehyde (565)	25.29 (1.377)	EI		37	14	[c]			9		
	25.21 (1.378)	Methane CI		5	54	[c]	10				
	25.23 (1.378)	PFBOH CI		100	64	[c]	17		[b]	[b]	[b]

[a] Blanks indicate that ions were absent or <1% relative intensity.
[b] *m/z* 181 is a reagent ion of PFBOH. Thus, in this mode of ionization, the mass range detected was *m/z* 230 to *m/z* 650.
[c] The *m/z* of the $(M+181)^+$ ion is greater than the mass range of the instrument, and thus could not be detected.
Boldface values were reported by Yu et al. [14].

silyl group. These ions establish the presence of a hydroxy or carboxy group on the PFBHA derivative [11,14,15]. For the model compounds examined in this study, the percent relative intensities of the *m/z* 73 and *m/z* 75 ions range from 24–100%, and 8–37%, respectively. In addition, a *m/z* 147 fragment ion corresponding to $(CH_3)_2Si{=}O{-}Si(CH_3)_3^+$ is characteristic in the EI mass spectra of compounds contain-

Table 4
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBHA/BSTFA derivatives of oxo acids.

Compound (molecular weight of derivative)	Retention time (relative retention time)	Mode of ionization	Ion (% relative intensity)[a]							
			$(M-H)^+$	$(M)^+$	$(M+H)^+$	$(M+181)^+$	$(M-15)^+$	*m/z* 181	*m/z* 75	*m/z* 73
Pyruvic Acid (355)	16.39 (0.893)	EI		–; **9**			26; **24**	100; **100**	6; 7	50; **60**
	16.31 (0.892)	Methane CI		5	100; **83**	1; **12**	34; **26**	4		21
	16.33 (0.892)	PFBOH CI		39	87	100	43	[b]	[b]	[b]
2-Ketobutyric Acid (269)	16.89 (0.920)	EI					31	100	11	70
	16.81 (0.919)	Methane CI	3	7	100	2	33			22
	16.83 (0.919)	PFBOH CI	7	35	77	100	41	[b]	[b]	[b]

[a] Blanks and dashes indicate that ions were absent or <1% relative intensity.
[b] Mass range detected was *m/z* 230 to *m/z* 650. Thus, ions were not detected in the PFBOH CI mass spectra.
Boldface values were reported by Yu et al. [14].

Table 5
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBBr derivatives of mono-carboxylic acids

Compound	Mode of ionization	Ion % (relative intensity)[a]						
		$(M-H)^+$	$(M)^+$	$(M+H)^+$	$(M+181-H)^+$	$(M+181)^+$	$(M-H+181)^+$	*m/z* 181
Acetic acid (240)	EI	2	8					100
	Methane CI	2	1					10
	PFBOH CI	32	100		6	1		[b]
Butyric acid (268)	EI	2						100
	Methane CI	2	2					100
	PFBOH CI	32	100	69	72	18		[b]
Valeric acid (282)	EI	3						100
	Methane CI	2; **8**	2					100
	PFBOH CI	100; **56**	22	58	69	22	5	[b]
Hexanoic acid (296)	EI						6	100
	Methane CI	5	2					100
	PFBOH CI	100	45	5				[b]
Octanoic acid (324)	EI							100
	Methane CI	2						88
	PFBOH CI	100	45	5				[b]
Decanoic acid (352)	EI							100
	Methane CI							34
	PFBOH CI	100	38	6				[b]

[a] Blanks indicate ions were absent or <1% relative intensity.

[b] Mass range detected was *m/z* 230 to *m/z* 650. Thus, ions were not detected in PFBOH CI mass spectra.

ing more than one trimethyl silyl group, and thus more than one hydroxyl group on the molecule. Molecular ion intensities are fairly weak for most of the compounds, ranging from 0–8% relative intensity, exclusive of the aromatic compounds. A range of 6–100% relative intensity was observed for the $(M-CH_3)^+$ ion. In most cases, the molecular weight of an unknown hydroxy carbonyl can be determined by first noting the presence of *m/z* 181, *m/z* 73, and *m/z* 75 fragment ions and then locating the $(M-CH_3)^+$ ion.

Charge exchange and proton transfer reactions are also evident in the methane CI ion trap mass spectra of the PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids. Again, the percent relative intensity of the $(M+H)^+$ ion was greater than the relative intensity of either the $(M-H)^+$ or $(M)^{+\cdot}$ ions, and ranged from 11–100%. The $(M+H)^+$ ion was the base peak in the methane CI mass spectra of pyruvic acid and 2-ketobutyric acid. We obtained reasonable agreement between these data and the data reported by Yu et al. [14]. Again, by using PFBOH as a chemical ionization reagent, we increased the formation of the $(M+181)^+$ ion. For certain compounds the percent relative intensity of the $(M+H)^+$ is lower in the PFBOH CI mass spectra compared to the methane CI mass spectra (e.g. for hydroxy acetone, 1-hydroxy-2-butanone, 4-hydroxybenzaldehyde, pyruvic acid, 2-ketobutyric acid). In these cases, we also observe a concomitant increase in the percent relative intensity of either or both the $(M-H)^+$ ion or $(M)^{+\cdot}$ ion.

3.4. PFBBr derivatives of carboxylic acids

For the pentafluorobenzyl derivatives of carboxylic acids, either the *m/z* 181 ion or another fragment ion is the base peak in the EI as well as the methane CI mass spectra. Accordingly, for carboxylic acids neither EI nor methane CI afford production of ions for unambiguous molecular weight determinations. The reaction of the PFBBr derivatives with PFBOH promotes the formation of a host of molecular and *pseudo* molecular ions including $(M-H)^+$, $(M)^+$, $(M+H)^+$, $(M+181)^+$, $(M+181-H)^+$ and $(M+181+H)^+$ ions. For the mono-carboxylic acids, either the $(M-H)^+$ or $(M)^{+\cdot}$ ions are the base peak. Greater internal energies appear to be imparted to the

Table 6
Effect of mode of ionization on production of molecular and *pseudo*-molecular ions for PFBBr derivatives of alkeonic and di-carboxylic acids

Compound	Mode of ionization	$(M - H)^+$	$(M)^+$	$(M + H)^+$	$(M + 181 - H)^+$	$(M + 181)^+$	$(M + 181 + H)^+$	$(M - 181)^+$	*m/z* 181
Alkenoic acids									
Acrylic acid	EI		26						100
(252)	Methane CI	2	4; **10**	–; **2**		–; **1**			100; **100**
	PFBOH CI	11; **14**	100; **100**	14; **11**	5	–; **2**			[b]
Methacrylic	EI		28	5					100
acid (266)	Methane CI		8; **19**	36; **79**		–; **11**			100; **100**
	PFBOH CI	6; **5**	100; **48**	53; **100**	7	14; **38**	3		[b]
Di-acids									
Succinic	EI								100
	Methane CI	–; **3**	–; **21**	–; **100**					100
	PFBOH CI		19	100					[b]
Glutaric acid	EI								100
	Methane CI		1	1					100
	PFBOH CI		3	17					[b]
Adipic acid	EI								100
	Methane CI								100
	PFBOH CI	4	7	47					[b]

[a] Blanks indicate ions were absent or <1% relative intensity.
[b] Mass range detected was *m/z* 230 to *m/z* 650. Thus, ions were not detected in the PFBOH CI mass spectra.
Boldface values were reported by Chien et al. [14].

dicarboxylic acids, because the $(M - 197)^+$ ion is the base peak in the mass spectra of glutaric and adipic acid (not shown). The intensity of the $(M + H)^+$ for these compounds, however, may be sufficient (17% for glutaric acid and 47% for adipic acid) to enable molecular weight determinations. For the few mass spectra of derivatives characterized in this study and the study conducted by Chien et al. we are unable to conclude any clear advantage of using methane with PFBOH.

3.5. Investigation of ion/molecule reactions

The observation of $(M - H)^+$, $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$ ions in the PFBOH chemical ionization mass spectra indicate that PFBOH reagent ions act to effect hydride ion abstraction, charge exchange, proton transfer, and adduction reactions. The mass spectrum of PFBOH is characterized by the predominance of three ions: a $(M)^{+\cdot}$ ion at *m/z* 198 $(C_6F_5CH_2OH)^+$ that exists at 58% relative intensity; a $(M - H)^+$ ion at *m/z* 197 $(C_6F_5CH_2O)^+$ that exists at 22% relative intensity; and the pentafluorobenzyl cation at *m/z* 181 $(C_6F_5CH_2)^+$ that is the base peak in the mass spectra [see Fig. 2(A)]. To explain the reactions observed in the PFBOH chemical ionization mass spectra, we hypothesized the following reactions:

(1) Adduct formation

$$C_6F_5CH_2^+ + M \rightarrow MC_6F_5CH_2^+$$
$$(m/z\ 181)$$

(2) Proton transfer

$$C_6F_5CHOH^+ + M \rightarrow C_6F_5CHO + (M + H)^+$$
$$(m/z\ 197)$$

(3) Charge exchange

$$C_6F_5CH_2OH^{+\cdot} + M \rightarrow C_6F_5CH_2OH + (M)^{\cdot+}$$
$$(m/z\ 198)$$

(4) Hydride ion abstraction

$$C_6H_5CH_2OH^{+\cdot} + M \rightarrow C_6F_5CHOH_2 + (M{-}H)^+$$
$$(m/z\ 198)$$

We tested this hypothesis by conducting experiments in which a reagent ion was isolated prior to reaction with pentafluorobenzyl derivatives of representative

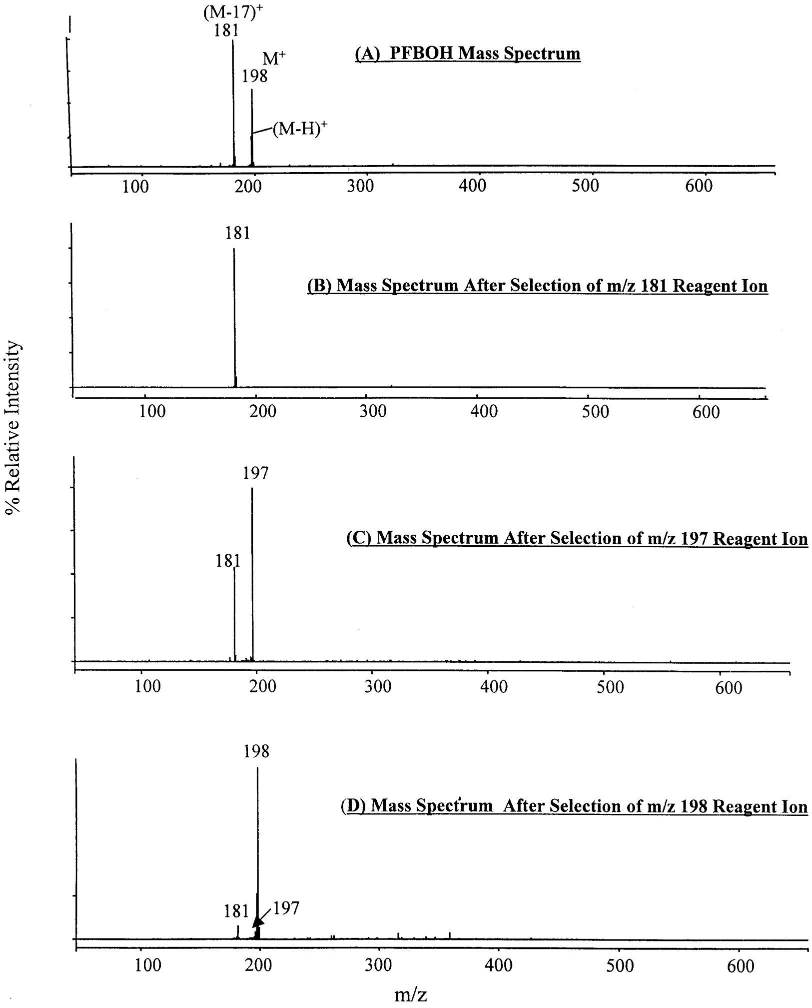


Fig. 2. PFBOH mass spectrum (A) and mass spectra after selection of reagent ions (B), (C), (D).

aromatic aldehydes, dicarbonyls, hydroxy carbonyls, and oxo acids. Ions with *m/z* below the selected reagent ion were ejected by ramping the rf field amplitude with axial modulation applied to the endcap electrodes. Ions above the *m/z* of the selected reagent ion were ejected by applying a broadband multifrequency waveform (i.e. a resonant ejection/broadband ejection method). A 1 *m/z* mass isolation window was employed to isolate the *m/z* 197 and 198 ions, and a 1 ms isolation time was utilized to minimize fragmentation of the ions. Under such conditions, we were able to nearly isolate the *m/z* 181 ion but could not isolate the *m/z* 197 ion from the *m/z* 181 ion; and the *m/z* 198 ion from the *m/z* 197 and 181 ions [Fig. 2(B), (C), and (D)]. Nonetheless, by comparing the percent relative intensities of the molecular and *pseudo*-molecular ions, insight can be gained into the reactions affecting the formation of these ions.

In the mass spectra in which the *m/z* 181 ion was selected, only a minor amount (1% relative intensity) of the *m/z* 198 ion was present, and the absolute intensity of the *m/z* 181 ion was similar to the absolute intensity observed in the PFBOH mass spectrum acquired prior to the performance of the experiment. The presence of the *m/z* 198 ion, and the employment of nominal mass resolution indicate that the *m/z* 181

Table 7
Comparison of relative intensity of molecular and *pseudo*-molecular ions of PFBHA derivatives generated by reaction with selected reagent ions

	Reagent ion selected (% relative intensity)	Other ions (% relative intensity)	$(M - H)^+$	$(M)^+$	$(M + H)^+$	$(M + 181)^+$	$(M + 181 - H)^+$
o-Tolualdehyde	None		**6**	**60**	**43**	**100**	**1**
	m/z 181 (100)			1	3	**100**	**1**
	m/z 197 (100)	*m/z* 181 (71)		9	**100**	33	
	m/z 198	*m/z* 181 (7); *m/z* 197 (10)	5	*35*	16	75	
3-Nitrobenzaldehyde	None		**12**	**17**	**24**	**100**	
	m/z 181 (100)					**100**	
	m/z 197 (100)	*m/z* 181 (71)		**4**	**100**	39	
	m/z 198 (100)	*m/z* 181 (7); *m/z* 197 (10)	*29*	**48**	38	12	
Glyoxal	None		**12**	**99**	**56**	**100**	**20**
	m/z 181 (100)			2	2	**100**	21
	m/z 197 (100)	*m/z* 181 (71)	3	7	**100**	46	14
	m/z 198 (100)	*m/z* 181 (7); *m/z* 197 (10)	*3*	**36**	8	100	18

ion is a fragment of the *m/z* 198 ion. We were able to isolate the *m/z* 197 ion from the *m/z* 198 ion, but unable to completely eliminate the presence of the *m/z* 181 ion. Again, since we operated under nominal mass resolution conditions, the data infer that the *m/z* 181 ion is also a fragment of the *m/z* 197 ion. The mass-selected *m/z* 197 ion mass spectrum was thus comprised of the *m/z* 197 (100% relative intensity) and the *m/z* 181 (71% relative intensity) ions. We were also unable to isolate the *m/z* 198 ion from the *m/z* 197 and 181 ions. The resulting mass spectrum was comprised primarily of the *m/z* 198 ion (100% relative intensity) with minor amounts of the *m/z* 197 (20% relative intensity) and *m/z* 181 (7% relative intensity ions). For the same reasons given previously, these data suggest that fragmentation of the *m/z* 198 yields the *m/z* 197 ion, which in turn fragments to produce the *m/z* 181 ion.

Because complete isolation of the *m/z* 197 and *m/z* 198 ions was not accomplished, the reactions of these ions were inferred by comparing differences in the percent relative intensities of the ions generated by each experiment, to each other, and to the PFBOH CI mass spectra. The data are presented in Table 7. The percent relative intensities of each ion in the PFBOH CI ionization mass spectra are boldface. The intensity of ions that are attributed to either the *m/z* 181, 197, or 198 reagent ions are boldface and italicized. As an example of our analyses, we present the PFBOH chemical ionization mass spectrum, and the mass spectrum resulting after isolation of the *m/z* 198, 197, and 181 ions for the PFBHA derivative of glyoxal in Fig. 3. The PFBOH chemical ionization mass spectrum of the derivative is presented in the top [Fig. 3(A)] mass spectra. Present are $(M + 181)^+$, $(M - H + 181)^+$, $(M + H)^+$, $(M)^{+\cdot}$, and $(M - H)^+$ ions at 100%, 20%, 56%, 99%, and 12% relative intensities, respectively. The mass spectra resulting after isolation of the *m/z* 181 ion is presented in [Fig. 3(B)]. $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$ ions are present at 2%, 2%, and 100%. The predominance of the $(M + 181)^+$ ion demonstrates that the *m/z* 181 ion effects formation of the $(M + 181)^+$ ion. The presence of *m/z* 197 and *m/z* 181 ions generates $(M)^{+\cdot}$, $(M + H)^+$, and $(M + 181)^+$, and $(M - H + 181)^+$ ions at relative intensities of 7%, 100%, 46%, and 14%, respectively [Fig. 3(C)]. The greater relative intensity of the $(M + H)^+$ ion compared to the previous mass spectrum [Fig. 3(B)] suggest that the *m/z* 197 ion effects transfer of a proton to the neutral analyte molecules. The similar and relatively low intensity of the $(M)^{+\cdot}$ ion between these spectra (7% and 2%) deters inference about the formation of this ion. The $(M - H)^+$, $(M)^{+\cdot}$, $(M + H)^+$, $(M + 181)^+$, and

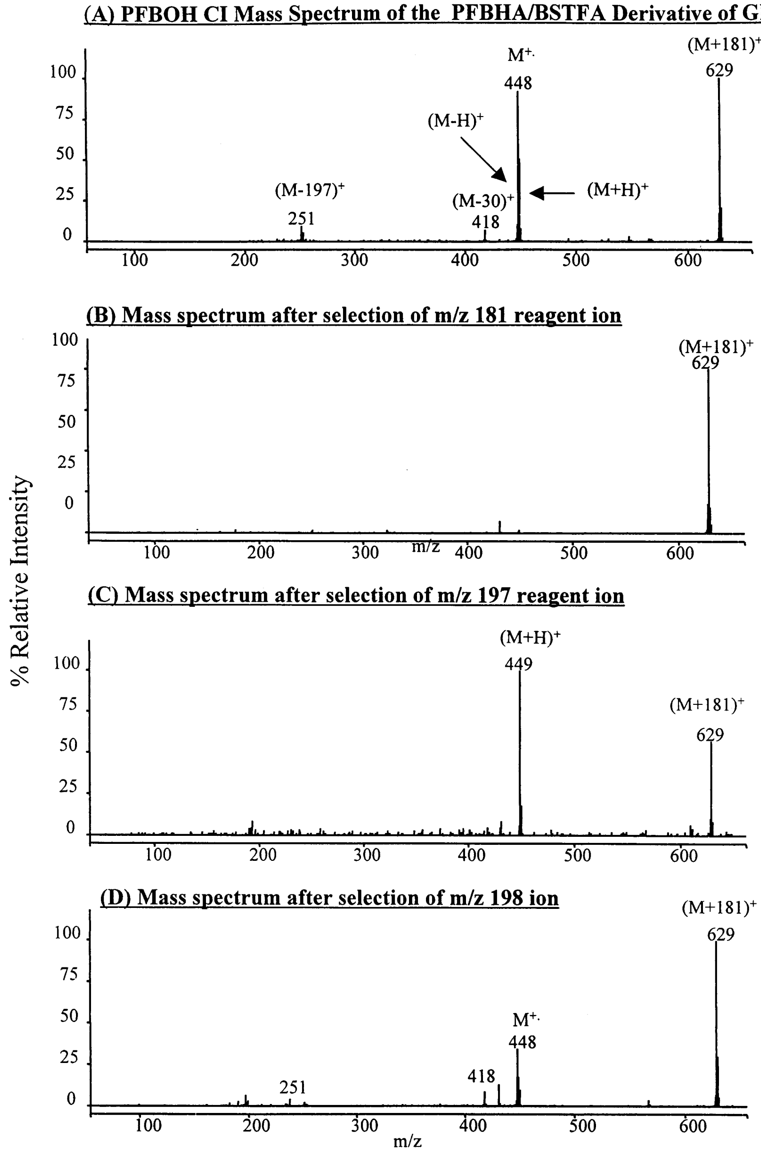


Fig. 3. PFBOH CI mass spectrum of glyoxal (A) and mass spectrum after selection of reagent ions (B), (C), (D).

$(M + 181 + H)^+$ are present at 3%, 36%, 8%, 100%, and 26% relative intensities in the mass spectrum obtained after isolation of the *m/z* 198 ion [Fig. 3(D)]. Because the $(M)^+$ ion is at a higher relative intensity in these mass spectra than in the *m/z* 181 or the *m/z* 197 ion selected mass spectra, these data suggest that the *m/z* 198 ion effects charge exchange reactions. Because the $(M + 181)^+$ ion is the base peak and the *m/z* 181 reagent ion was present in small amounts, this suggests that adduct formation is a facile reaction. Two exceptions are noted. For the PFBHA/BSTFA (Table 8) derivatives of 1,3-dihydroxyacetone and 2-ketobutyric acid, high relative intensities of the $(M)^{\cdot +}$ ion were also observed when the *m/z* 197 ion was the primary reagent ion. The data obtained for the PFBHA derivative of nitrobenzaldehyde and the

Table 8
Comparison of relative intensity of molecular and *pseudo*-molecular ions of PFBH/BSTFA derivatives generated by reaction with selected reagent ions

	Reagent ion selected (% relative intensity)	Other ions (% relative intensity)	$(M - H)^+$	$(M)^+$	$(M + H)^+$	$(M + 181)^+$	$(M + 181 - H)^+$
Hydroxy acetone	None		**8**	**16**	**100**	**98**	**2**
	m/z 181 (100)				6	**100**	
	m/z 197 (100)	*m/z* 181 (71)	5	**15**	**100**		
	m/z 198	*m/z* 181 (7); *m/z* 197 (10)	**100**	*30*	87		
1-Hydroxy-2-Butanone	None		**2**	**13**	**95**	**100**	
	m/z 181 (100)				4	**100**	
	m/z 197 (100)	*m/z* 181 (71)		**100**	**88**		
	m/z 198 (100)	*m/z* 181 (7); *m/z* 197 (10)		11	100		
4-Hydroxybenzaldehyde	None		**5**	**100**	**46**	**99**	
	m/z 181 (100)			12	6	**100**	
	m/z 197 (100)	*m/z* 181 (71)	14	41	**100**		
	m/z 198 (100)	*m/z* 181 (7); *m/z* 197 (10)	9	**100**	60		
1,3-Dihydroxyacetone	None		**15**	**24**	**73**	**100**	**12**
	m/z 181		9	3	4	**100**	**12**
	m/z 197	*m/z* 181 (71)		**45**	**100**	11	
	m/z 198	*m/z* 181 (7); *m/z* 197 (10)		22	9		
2-Ketobutyric acid	None			**44**	**47**	**100**	
	m/z 181					**100**	
	m/z 197	*m/z* 181 (71)		67	**100**	11	
	m/z 198	*m/z* 181 (7); *m/z* 197 (10)		32	**100**		

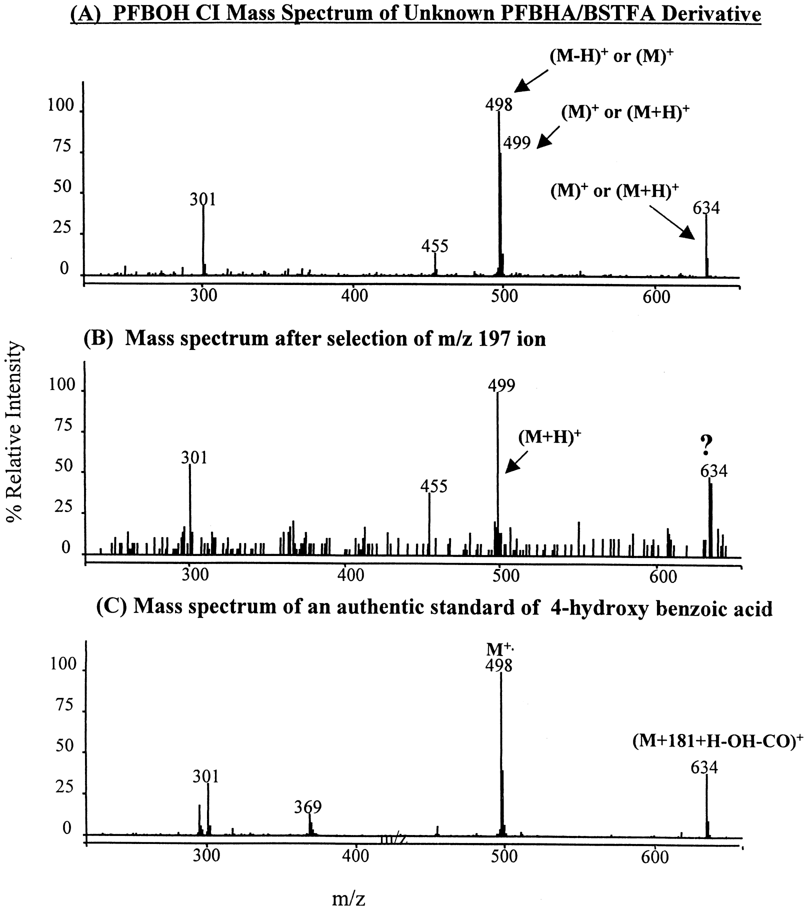
PFBHA/BSTFA derivative of hydroxy acetone also indicate the *m/z* 198 ion may promote hydride abstraction reactions for certain compounds.

These data demonstrate PFBOH reagent ions react to affect a complexity of reactions. Such reactions include adduct formation, hydride abstraction, proton transfer, and charge exchange. The *m/z* 181 reagent ion effects the production of $(M + 181)^+$ ions as expected. The presence of higher intensity $(M + H)^+$ ions in mass spectra in which the *m/z* 197 was the predominant reagent ion strongly suggests that the *m/z* 197 ion acts to transfer a proton to neutral analyte molecules. Similarly, we can infer that the *m/z* 198 ion primarily affects charge exchange and hydride abstraction reactions because the intensities of the $(M)^{+\cdot}$ and $(M - H)^+$ ions are greater than in the mass spectra generated after near isolation of the *m/z* 198 ion than in the other reagent ion selected mass spectra. Such reactions likely depend on the recombination energy, the proton affinity, and the hydride affinity of these reagent ions and the derivatives. Neither absolute nor relative physical–chemical constants exist for PFBOH and the pentafluorobenzyl derivatives, however, to further explore the gas phase ion chemistry.

3.6. Practical aspects of reagent ion selection

The complexity of reactions that produce $(M - H)^+$, $(M)^{+\cdot}$, $(M + H)^+$, $(M + 181)^+$, and $(M - H + 181)^+$ ions in the PFBOH chemical ionization mass spectra can make it difficult to identify the molecular weight of the derivative. By using our knowledge about ion/molecule reactions effected by PFBOH reagent ions, we were able to conduct experiments to identify a compound in an extract of fine particulate matter. This sample was obtained from the heavy duty (diesel) bore of the Caldecott tunnel, a traffic tunnel between Walnut Creek and Berkeley, California.

From our knowledge of the reaction of PFBOH with pentafluorobenzyl bromide derivatives of carboxylic acids, we attempted to interpret the PFBOH chemical ionization mass spectra presented in Fig. 4(A).


(A) PFBOH CI Mass Spectrum of Unknown PFBHA/BSTFA Derivative

(B) Mass spectrum after selection of m/z 197 ion

(C) Mass spectrum of an authentic standard of 4-hydroxy benzoic acid

Fig. 4. PFBOH CI mass spectra of an unknown in a fine particulate extract of diesel exhaust and PFBOH CI mass spectrum of an authentic standard of 4-hydroxybenzoic acid.

Because $(M - H)^+$, $(M)^{+\cdot}$, and $(M + H)^+$ ions can be generated by the reaction of PFBOH with PFBBr derivatives, we were uncertain about the relationship between the *m/z* 498 and *m/z* 499 ions in the mass spectrum. We were also confused by the presence of an ion at *m/z* 634. Addition of a pentafluorobenzyl group to molecules with masses of 498, 499, or 634 would generate $(M + 181)^+$ ions above the mass range of our instrument, and thus would not be detected. To determine which of these ions is the molecular ion of the compound, we conducted an experiment in which the *m/z* 197 ion was mass selected to produce $(M + H)^+$ ions. The resulting mass spectrum presented in Fig. 4(B) suggests that the *m/z* 498 corresponds to an $(M)^{+\cdot}$ ion. We thus tentatively identified the compound as 4-hydroxybenzoic acid, and confirmed the identity through the analysis of an authentic standard. We conjecture that the *m/z* 634 ion arises from the generation of an $(M + 181 + H)^+$ ion and loss of a hydroxyl group and CO from this adduct ion. Because of the restricted mass range (*m/z* 650) of our instrument we could not explore this hypothesis.

4. Conclusions

Four previous studies demonstrated the power of pentafluorobenzyl derivatization in combination with ion trap mass spectrometry to identify novel photooxidation products in chamber studies [9,10,12,14]. This knowledge led to advances in understanding photochemical reaction mechanisms that, in turn, can be incorporated into photochemical airshed models devised to understand the impact of hydrocarbon emissions on air quality. The inaccuracies of models developed in this manner (i.e. without field validation) do not become evident until attempts to link chamber and ambient air data are unsuccessful. Hence, field measurements are critical for validating air quality models, as well as for understanding processes in the environment that affect the generation and fate of polar organic compounds. Ambient measurements of oxygenated and polar organics, particularly the multifunctional species, have been difficult, due to absence of suitable methodologies. To this end, in this and a previous study, we demonstrated that the "tools" utilized in chamber studies can also be employed to measure oxygenated and polar organics in air and particulate samples [15].

Through the characterization of the EI, methane CI, and PFBOH mass spectra of PFBHA derivatives of aldehydes, ketones, and dicarbonyls, PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids, and PFBBr derivatives of carboxylic acids, we establish the power of PFBOH to enhance the formation of molecular and *pseudo*-molecular ions. In addition, where possible, we compared our results with previous studies. We obtained good agreement between our work and the work of others. This result indicates that the results are reproducible among laboratories. From characterization of the PFBOH mass spectra, we realized that PFBOH reacts to effect adduct formation, proton transfer, charge exchange, and hydride abstraction reactions. By conducting experiments in which reagent ions were selected prior to their reaction, we explored these reactions. The results establish that ion/molecule reactions between the *m/z* 181 reagent ion and neutral analyte molecules effect the formation of an $(M + 181)^+$ ion. The data also suggest that the *m/z* 197 ion effects proton transfer reactions, and that the *m/z* 198 ion generates $(M)^{\cdot +}$ and $(M - H)^+$ ions. It is difficult to fully comprehend the fundamentals of these reactions without physical–chemical constants for PFBOH and the derivative molecules. Nonetheless, through this and our previous work, we establish the practicality and need to employ PFBOH to identify pentafluorobenzyl derivatives. In addition, we demonstrate the utility and value of selecting certain reagent ions to effect the production of specific ions to facilitate unambiguous molecular weight determinations.

Acknowledgements

We thank Bob Brittain and Gary Bauer (Varian Chromatography Systems) for helpful discussions, Ed Nygren (Varian Chromatography Systems) for his technical assistance, and Robert Flochinni for use of the IMPROVE sampler. We also thank the California Air Resources Board (Contract No. 96-303) and the American Society for Mass Spectrometry and the University of California, Davis for supporting the work.

References

[1] B.J. Turpin, J.J. Huntzicker, Atmos. Environ. (1995) 3527.
[2] J.R. Odum, T.P.W. Jungkamp, J.R. Griffin, H.J.L. Forstner, R.C. Flagan, J.H. Seinfeld, Environ. Sci. Technol. 31 (1997) 1890.
[3] H.J.L. Forstner, R.C. Flagan, J.H. Seinfeld, Environ. Sci. Technol. 31 (1997) 1345.
[4] P. Saxena, L.M. Hildemann, P.H. McMurry, J.H. Seinfeld, J. Geophys. Res. 100 (1995) 18 755.
[5] W.F. Rogge, M.A. Mazurek, L.M. Hildemann, G.R. Cass, B.R.T. Simoneit, Atmos. Environ. 27A (1993) 1309.
[6] P. Saxena, L.M. Hildemann, J. Atmos. Chem. 24 (1996) 57.
[7] R.J. O'Brien, J.H. Crabtree, J.R. Holmes, M.C. Hoggan, A.H. Bockian, Environ. Sci. Technol. 9 (1975) 577.
[8] T. Pickle, D.T. Allen, S.E. Pratsinis, Atmos. Environ. 24A (1990) 2221.
[9] J. Yu, H.E. Jeffries, R.M. Le Lacheur, Environ. Sci. Technol. 29 (1995) 1923.
[10] J. Yu, H.E. Jeffries, K.E. Sexton, Atmos. Environ. 31 (1997) 2261.
[11] R.M. Le Lacheur, L.B. Sonnenberg, P.C. Singer, R.F. Christman, M.J. Charles, Environ. Sci. Technol. 27 (1993) 2745.
[12] C.J. Chien, M.J. Charles, K.G. Sexton, H.E. Jeffries, Environ. Sci. Technol. 32 (1998) 299.
[13] W.H. Glaze, M. Koga, D. Cancilla, Environ. Sci. Technol. 23 (1989) 838.
[14] J. Yu, R.C. Flagan, J.H. Seinfeld, Environ. Sci. Technol. 32 (1998) 235.
[15] R.S. Spaulding, P. Frazey, X. Rao, M.J. Charles (unpublished).