Identifying Airborne Carbonyl Compounds in Isoprene Atmospheric Photooxidation Products by Their PFBHA Oximes Using Gas Chromatography/Ion Trap Mass Spectrometry

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Coupled with gas chromatographic/mass spectrometric detection, the oxime formation of aldehydes and ketones by reaction with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) can be used to determine multi-functional airborne carbonyls as well as simple carbonyls. In this study, we report that methane chemical ionization of the PFBHA-carbonyl derivatives in an ion trap mass spectrometer provides for the determination of molecular weights of unknown carbonyls. We first report the study of model carbonyl compounds and then illustrate examples of detecting and identifying carbonyl products from methyl vinyl ketone and methacrolein experiments conducted in an indoor irradiation chamber and from isoprene experiments conducted in a dual outdoor smog chamber. The examples show that multi-functional carbonyls do account for part of the missing reaction products in the atmospheric oxidation of isoprene. The advantages of PFBHA derivatives over the normally used 2,4-dinitrophenylhydrazine (DNPH) derivatives will also be discussed.

Introduction

Carbonyls (ketones and aldehydes) are important in atmospheric chemistry. They are commonly detected as products of incomplete combustion and are almost obligatory intermediates in the atmospheric oxidation of organic compounds (1). Further, by their photolysis reactions, some carbonyls are important in initiating and sustaining the photochemical radical pool necessary to produce tropospheric ozone. Detecting and measuring the various carbonyl compounds are essential steps to understanding

and elucidating the relative importance of various fates and reactions related to hydrocarbon and carbonyl compounds in the atmosphere and, hence, to formulating cost-effective control strategies for photochemical oxidants.

It has been reported that the detected atmospheric oxidation products of many hydrocarbons fail to account for all the reacted hydrocarbon. For example, the products clearly identified from isoprene's photooxidation process are formaldehyde, methacrolein, methyl vinyl ketone, and 3-methylfuran, and these only account for 55–65% of reacted isoprene (2–4). A number of other hydroxy carbonyl compounds have been proposed (5, 6) to account for the shortfall. The results of our study shows that multifunctional carbonyls do contribute to the missing carbon in the oxidation of isoprene but not some of those previously proposed.

Calvert and Madronich's (7) theoretical study of the initial products of the atmospheric oxidation of hydrocarbons indicated that carbonyls comprise 79% and 89% of alkane and alkene oxidation products in a NO_x-rich atmosphere. A challenging task is to identify the numerous carbonyls that might be encountered in a complicated atmospheric system. The most often used current method for analysis of carbonyls is to derivatize them using 2,4-dinitrophenylhydrazine (DNPH), followed separation by high-performance liquid chromatography (HPLC), and to use ultraviolet absorbance to detect the derivatives (8, 9). The DNPH derivatizing technique, however, fails to distinguish α-hydroxy carbonyls and the corresponding dicarbonyls, thus confusing glycolaldehyde and glyoxal (or hydroxyacetone and methylglyoxal) because these form the same osazone when the derivatization reaction proceeds in an organic solvent (10–13). Derivatization in aqueous phase gives rise to distinctive derivatives but suffers low sensitivity and poor resolution for these two types of carbonyls (14–17). Unfortunately, these two types of compounds are often present simultaneously in the atmospheric oxidation of hydrocarbons. Another problem with DNPH-HPLC techniques has been coelution or poor resolution of similar carbonyls such as acrolein, acetone and propanal, and methyl ethyl ketone and butanal (18, 19). In addition, identification of unknown carbonyls by the DNPH method is difficult, even if coupled with a secondary method such as multiple columns or mass spectrometry.

To circumvent the difficulties encountered with the DNPH method, we explored other methods for detecting airborne carbonyls. We found the oxime formation of aldehydes and ketones by reaction with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) coupled with gas chromatography/mass spectrometric detection (GC/MS) offers an excellent alternative to the DNPH-HPLC method. The PFBHA-GC/MS or GC/ECD (electron capture detection) method has been successfully used to quantify carbonyls in aqueous environmental samples and carbonyl-containing compounds such as keto steroids, prostaglandins, and thromboxanes in biological samples (20–25). The application of this method to airborne carbonyls has been very limited. Le Lacheur et al. (26) reported that the GC/MS analysis of carbonyl-PFBHA oximes offers an approach to identify unknown carbonyl

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TABLE 1

GC Retention Times and CI Mass Spectra of PFBHA Derivatives of Model Carbonyl Compounds

carbonyl	RT	181	M	M + 1	M + 29	M + 41	M + 181	M − 17	M − 30	M − 181	M − 197
Monofunctional Aldehydes											
formaldehyde	17.37	100	4.3	88.3	6.4	3.1	29	0.1	9.1	na[a]	na
acetaldehyde	19.50	10.1	4.1	100.0	6.6	1.5	8.4	0.1	2.1	0.2	na
	19.68	7.2	3.6	100.0	6.7	1.5	7.0	0.0	1.2	0.1	na
propanal	21.17	12.6	2.6	100.0	7.8	2.1	2.5	3.9	1.6	0.3	24.9
	21.28	25.2	2.3	100.0	10.8	2.8	3.0	6.6	1.8	0.3	27.6
butanal	22.76	8.4	4.2	100.0	9.2	2.7	3.4	0.9	0.0	0.5	13.8
	22.86	25.0	3.4	100.0	12.9	3.1	6.4	3.3	0.0	0.2	33.1
2-butenal	23.72	6.5	2.6	100.0	5.3	2.0	6.6	0.4	10.2	1.0	39.0
	23.86	17.8	2.6	100.0	5.5	2.3	10.6	0.7	11.7	1.8	32.8
methacrolein	22.50	6.6	5.7	100.0	1.8	1.0	3.9	1.5	3.0	3.8	36.2
Monofunctional Ketones											
acetone	20.77	2.3	6.8	100.0	12.3	3.1	1.6	2.4	2.6	0.2	97.5
methyl ethyl ketone	22.20	3.2	2.5	69.6	12.4	2.3	0.9	6.5	0.0	0.2	100.0
	22.26	2.1	2.9	100.0	13.5	2.5	1.1	6.6	0.0	0.1	26.2
methyl vinyl ketone	20.21	5.9	7.4	100.0	7.3	1.5	8.6	0.6	4.8	1.1	70.5
3-pentanone	23.42	1.7	2.5	100.0	14.8	2.2	1.3	6.4	0.0	0.8	21.5
2-pentanone	23.44	3.7	2.7	75.8	15.3	2.8	0.6	1.1	0.0	0.7	100.0
	23.59	1.4	3.2	100.0	14.0	2.9	0.8	0.7	0.1	0.7	4.1
Hydroxy Carbonyls											
glycolaldehyde	23.95	29.8	1.9	9.8	0.3	0.8	4.3	100.0	1.1	0.1	3.7
	24.28	42.6	1.6	15.5	0.2	0.9	1.3	100.0	1.7	0.2	8.2
hydroxyacetone	24.73	8.2	1.4	27.1	1.8	0.9	7.6	100.0	0.9	0.1	1.3
	24.93	100.0	6.2	85.0	0.8	1.4	4.0	90.1	6.6	2.1	57.0
3-hydroxy-2-butanone	25.02	4.1	53.8	7.2	0.4	0.1	1.1	100.0	0.0	0.0	1.5
1-hydroxy-2-butanone	25.74	9.7	1.2	27.7	2.2	0.8	6.5	100.0	0.2	0.1	1.4
100% = m/z 56	25.91	21.1	1.5	46.3	1.5	0.3	1.1	22.8	0.4	0.0	44.9
Dicarbonyls											
glyoxal	31.84	22.9	4.2	100.0	7.2	1.4	16.8	2.0	1.8	0	3.6
	32.05	11.2	3.6	100.0	2.6	0.5	9.3	6.3	1.9	0.2	6.0
methylglyoxal	31.55	100.0	0.0	65.3	7.7	0.0	0	5.5	0.0	17.7	57.9
	32.00	22.8	1.4	100.0	12.5	1.9	7.9	0.3	1.0	1.1	31.5
	32.39	100.0	0.0	87.7	12.2	2.3	2.9	0.0	2.4	9.3	29.9
	32.53	9.1	1.6	100.0	4.8	0.6	4.9	12.1	0.9	0.6	11.8
2,3-butandione	31.71	46.0	0.0	83.3	8.7	1.8	na	0.0	0.0	1.2	100.0
	33.12	7.8	1.5	100.0	6.5	0.7	na	2.1	0.1	0.1	11.2
2,4-pentadione	31.80	100.0	0.0	56.5	2.0	0.0	na	0.0	0.0	0.1	61.7
	33.56	11.6	1.5	100.0	6.6	2.0	na	0.0	0.0	0.2	91.5
100% at m/z = 252	33.97	6.2	0.8	57.6	2.8	1.2	na	0.0	0.0	0.0	41.8

[a] na, data not available due to outside mass range selected.

compounds. In this study, we found that the chemical ionization (CI) of the PFBHA-carbonyl derivatives in an ion trap mass spectrometer (MS/IT) provides substantial molecular ion information from which we can determine the molecular weight of unknown carbonyls. We report here studies of model carbonyl compounds and give examples of detecting and identifying carbonyl products from outdoor and indoor smog chamber experiments of isoprene and its major products, methyl vinyl ketone (MVK) and methacrolein (MACR).

Materials and Methods

Model Compound Studies. A series of model compounds including simple monofunctional carbonyls, unsaturated carbonyls, hydroxy carbonyls, and dicarbonyls were chosen based on their possible relevance to the atmospheric oxidation processes (see Table 1). The derivatization procedure was adapted from the one described by Cancilla et al. (22). Approximately 1 mg/L aqueous solutions were made for each carbonyl compound. An excess amount of PFBHA aqueous solution (0.5 mL of 5 mg/mL solution) was added to 5 mL of the carbonyl solution. One drop of 37% hydrochloric acid (HCl) was added to lower the solution pH to about 2. The mixture was allowed to stand at room temperature for 24 h. Two drops of 37% HCl were added to further acidify the mixture just before 2 mL of hexane was added to extract the PFBHA derivatives. Most of the excess PFBHA remained in the acidic aqueous phase, thus avoiding the deterioration of the column and detection by excess PFBHA. About 50 mg of anhydrous Na_2SO_4 was added to the hexane extract to adsorb trace amounts of water remaining after separation. One microliter of the hexane extract was injected into a Varian Saturn II GC/MS/IT system operated with an MS-grade 60 m × 0.325 mm J&W DB-5 chemically bonded, fused-silica capillary column. The temperature program used was as follows: initial temperature 60 °C, held for 1 min; 60−100 °C at 5 °C/min; 100−280 °C at 10 °C/min; held at 280 °C for 10 min. The injector had an initial temperature of 60 °C and was kept at this temperature for 0.80 min. Then the injector temperature was raised to 250 °C at a rate of 180 °C/min and held at this temperature until the analysis was finished. The transfer line between the column and the ion trap was kept at 280 °C. The MS/IT can be readily operated in either EI (electron ionization) or CI mode, allowing back-to-back analysis of the same extract using different ionization modes. Methane was the CI reagent gas under CI mode. A mass scan range between 50 and 650 was chosen.
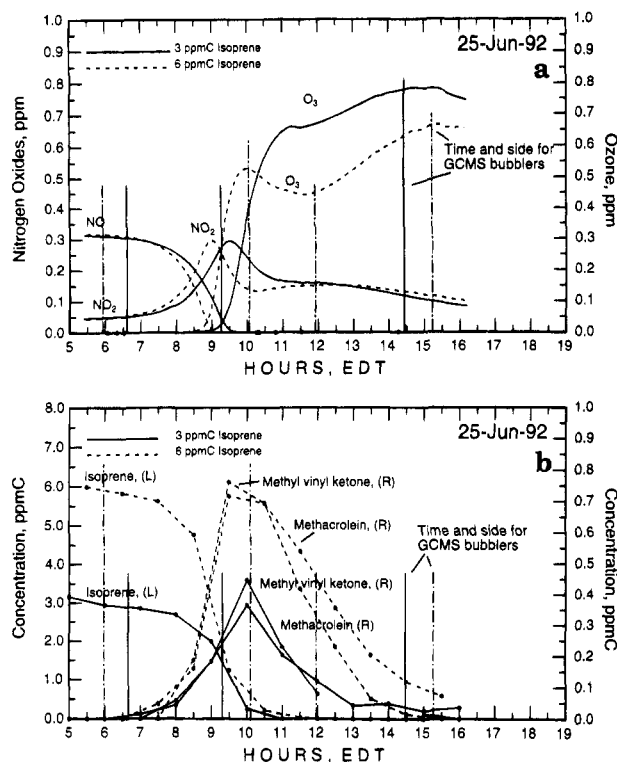
FIGURE 1. (a) Daytime dual outdoor smog chamber experiment using 3 and 6 ppm C isoprene and 0.37 ppm oxides of nitrogen. NO, NO₂, and O₃ time series for the two sides. Vertical lines mark times of bubbler samples for GC/MS analysis. (b) Daytime dual outdoor smog chamber experiment using 3 and 6 ppm C isoprene and 0.37 ppm oxides of nitrogen. Selected carbon-containing compounds measured by gas chromatography during the experiment. Vertical lines mark times of bubbler samples for GC/MS analysis.

Isoprene Outdoor Smog Chamber Experiments. Two outdoor smog chamber experiments using isoprene were conducted in a dual 150 m³ Teflon outdoor smog chamber located in a rural area in Pittsboro, NC (27). One was performed during the daytime in the presence of NO_x, and the other was during the nighttime in the presence of ozone.

In the daytime experiment conducted on June 25, 1992, one side of the chamber was injected with 3 ppm C isoprene and 0.37 ppm NO_x while the other side was injected with 6 ppm C isoprene and 0.37 ppm NO_x. All injections occurred before sunrise. Figure 1 reports the time series of the reactants and several products measured by continuous instruments and gas chromatographs. The daytime samples for GC/MS were collected by pulling chamber air into an impinger containing 20 mL of distilled water at a rate of 1 L/min for 30 min. The rest of the procedure was the same as the model carbonyl standards except that a 30-m column was used and 5–10 drops of 1 M pH 7 phosphate buffer solution was added before PFBHA addition.

In the nighttime experiment conducted on September 15–16, 1993, 2.5 ppm C of isoprene was injected initially into only one chamber, and ozone (O_3) was continuously injected into both chambers at 0.309 ppm/h over a period of 5 h. The nighttime samples were taken by pulling chamber air into an impinger containing 20 mL of distilled water at a flow rate of 0.56 L/min for 1 h. The collected samples were treated the same way as those in the model carbonyl standards.

Isoprene, MVK, and MACR Indoor Chamber Experiments. Experiments were conducted in a 300-L Teflon bag reactor (TBR) exposed at constant temperature (25 °C) to constant irradiation from a mixture of black lamps and sunlamps placed on both sides of the bag in an aluminum foil-lined box. The TBR was flushed and filled with clean air from a 250 L/min Aadco clean air generator. In a typical TBR experiment, 10 ppm C of organic compound, 10 ppm of NO, and either 5 ppm of methyl nitrite or 10 ppm of hydrogen peroxide to serve as a radical source were added to the filling stream. After the initial conditions had been established, the lights were turned on for up to 3 h of irradiation. A single sample was taken from the TBR throughout the irradiation period by pulling bag air into an impinger containing 20 mL of distilled water at a flow rate of 0.56 L/min. The collected samples were treated the same way as those in the model carbonyl standards.

Photolysis of hydrogen peroxide was used as the radical source in the MVK, MACR, and two isoprene TBR experiments. Photolysis of methyl nitrite is used as the radical source for one isoprene TBR experiments.

Results and Discussion

GC Separation and Mass Spectra of the Model Carbonyls. Satisfactory separation for most model carbonyl-PFBHA derivatives was achieved by utilizing the described chromatographic conditions, making it possible to analyze them within a single GC run. Similar carbonyls such as acetone and propanal are well separated. Except for symmetrical carbonyls such as formaldehyde and acetone, PFBHA forms two geometric isomers due to the rigid nitrogen–carbon double bond. More than two isomers are possible for dicarbonyls such as methylglyoxal (22). Some of the isomers, but not all of them, can be resolved by using the GC conditions described. α-Hydroxy carbonyls and the corresponding α-dicarbonyls such as glycolaldehyde and glyoxal and hydroxyacetone and methylglyoxal have distinctive derivatives and are well separated by the GC column under the conditions used.

As seen in previous studies (21, 26), the EI mass spectra of PFBHA oximes have a strong peak, usually a base peak, at m/z 181. This fragment ion is the pentafluorotropylium ion $C_6F_5CH_2^+$, originating from the derivatizing reagent PFBHA. Because of its intensity, the m/z 181 fragment ion provides an immediate indication of the presence of a carbonyl group in the original molecule and can be utilized to differentiate carbonyl compounds from other classes of organics in complex samples. The high intensity of this ion also makes it well suited for selected ion monitoring quantification.

In the ion trap, a molecular ion in the EI mass spectra is present for all the model compounds examined. However, the molecular ion is not always strong enough for an unambiguous molecular weight determination for aliphatic carbonyls. Le Lacheur et al. (26) reached a similar conclusion in their EI mass spectra analysis using the conventional double-focusing (EB) mass spectrometer.

The chemical ionization mass spectra data of model PFBHA derivatives are listed in Table 1. Figure 2 shows the full mass spectrum of the PFBHA derivative of methyl vinyl ketone as an illustration. All tested PFBHA derivatives show a strong protonated molecular ion MH⁺ with relative intensity ranging from 7% to 100%. The intensity of the MH⁺ ion for hydroxy carbonyls is considerably lower than other carbonyls. An ion with m/z = M − 197, loss of C_6F_5-CH_2O moiety from the neutral molecule, is consistently
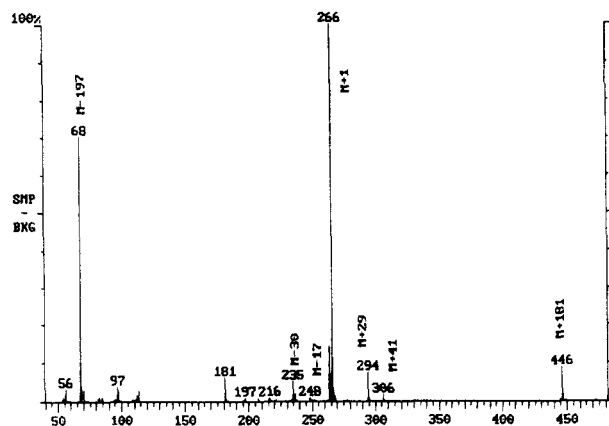
FIGURE 2. CI mass spectrum of O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivative of methyl vinyl ketone.
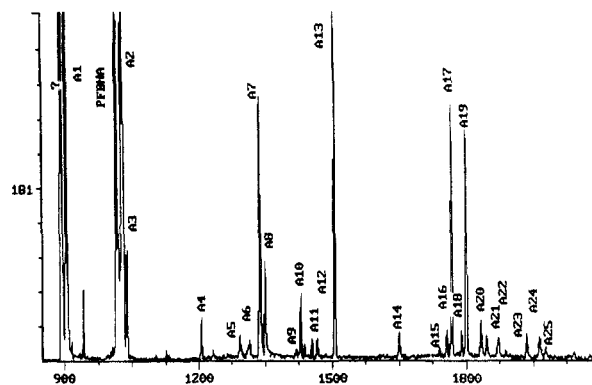

FIGURE 3. Reconstructed $m/z = 181$ ion chromatogram of a sample collected from a methacrolein indoor irradiated Teflon bag reactor experiment. Y-axis: intensity of $m/z = 181$ ion, X-axis: scan number.
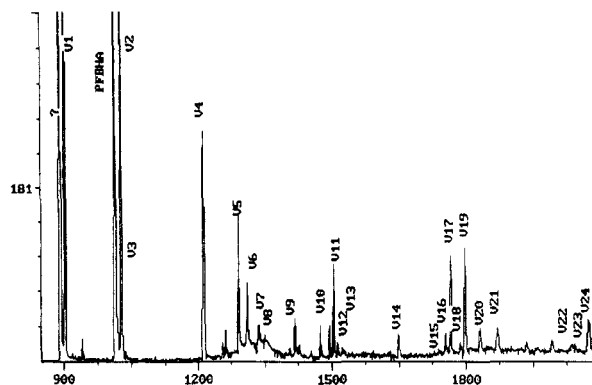

FIGURE 4. Reconstructed $m/z = 181$ ion chromatogram of a sample collected from a methyl vinyl ketone indoor irradiated Teflon bag reactor experiment. Y-axis: intensity of $m/z = 181$ ion, X-axis: scan number.

present with reasonably strong intensity (RI > 3%, except for hydroxy carbonyls). Some of the isomers of hydroxy carbonyl PFBHA derivatives have a relatively lower intensity ion at $m/z = M - 197$. Ions with $m/z = M + 29$ and $M + 41$, arising from the reaction of neutral molecule with the major reagent ions $C_2H_5^+$ and $C_3H_5^+$, are observed for all tested carbonyls. Ions with $m/z = M - 30$, $M - 181$, and $M - 211$, resulting from loss of NO, $C_6F_5CH_2$, and C_6F_5-CH_2ON, respectively, are observed for most tested compounds. These ions aid the determination of molecular weight of unknown carbonyls. In addition, a peak at $m/z = M + 181$ is also present to help confirm molecular weight diagnosis.

The adductive ion $[(M + 181)^+]$ results from a special principle of the ion trap mass spectrometer. The ion trap mass spectrometer holds ions in orbits in a chamber and uses a radio frequency (RF) field to separate and analyze ions. As the RF voltage is scanned upwards, ions of increasing mass to charge ratio become unstable and are ejected out the chamber. Before the ions are ejected, however, secondary ion–molecule reactions are possible. For the compounds examined here, the derivative molecules and the stable fragment ions $C_6F_5CH_2^+$ are abundant in the ion trap, and they have time to form ion adducts before the m/z 181 ions, i.e., $C_6F_5CH_2^+$, are ejected out the trap. We have observed, however, that when the analyte concentration is very low, the $[(M + 181)^+]$ ions are often below the detection limit.

The PFBHA derivatives of hydroxy carbonyls in CIMS have a strong characteristic peak at $m/z = M - 17$ (RI > 23%), corresponding to loss of OH from the molecular ion and/or loss of H_2O from MH^+ ions. Other carbonyl derivatives also show a peak at $M - 17$, but not so strong as hydroxy carbonyls (RI < 12%). Therefore, the presence of a strong ion of $M - 17$ is a useful but not conclusive indicator of the presence of a hydroxy group in addition to the carbonyl functional group. Further confirmation of the presence of the hydroxy group can be accomplished by a second derivatization step, e.g., derivatizing the hydroxy group using silylation reagents or methylation reagents. The disappearing of the original PFBHA derivative peak and the emerging of a new peak serve as evidence of the presence of a hydroxy group (26). We are currently investigating sequential reactions with bromine as a tool for the identification of unsaturated carbonyls and with periodic acid for the identification of α-hydroxy carbonyls.

Carbonyl Analysis in MVK/MACR Experiments. The presence of carbonyl products in both MACR and MVK

experiments was readily determined by examining the reconstructed ion chromatograms for the $m/z = 181$ ion (see Figures 3 and 4 and Tables 2 and 3). By comparing the retention time and the resulting CI mass spectra of the carbonyl products with those of the model compounds, we are able to identify formaldehyde, acetaldehyde, methacrolein, methyl vinyl ketone, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal, and biacetyl (2,3-butadione) in the samples. It is known that the reaction of MACR with OH radical forms hydroxyacetone and methylglyoxal and the reaction of MVK with OH radical leads to glycolaldehyde and methylglyoxal as major products (28, 29). Glyoxal can be produced as a result of OH radical reaction with glycolaldehyde (30). A trace amount of acetaldehyde is always detected in the distilled water blank. The formation pathway of biacetyl is not clear.

Two peaks, A10 and A13, in MACR and V11 in MVK TBR experiments were determined to have a molecular weight of 391, leading to the tentative identification of these peaks as pentafluorobenzaldehyde. An analysis of the pentafluorobenzaldehyde standard shows two peaks at the same retention times as A10 and A13, with the later peak being much stronger. The mass spectral data of the standard also agree well with the spectra in the MACR and MVK TBR samples. A low concentration of this compound might cause the weaker peak to be undetected, which explains why only the stronger peak in the MVK TBR sample was observed. This compound is a byproduct of the derivatizing process, resulting from PFBHA. Acidic conditions and a higher concentration of PFBHA favor the formation of this compound. The addition of pH 7 buffer accounts for the

TABLE 2

Carbonyl Products Detected in a Sample Collected from a Methacrolein Indoor Irradiated Teflon Bag Reactor Experiment (60-m Column)

peak no.	RT	identity	MW	comment
A1	17.38	formaldehyde	225	
A2	19.51	acetaldehyde	239	
A3	19.69	acetaldehyde	239	
A4	22.51	methacrolein	265	
A5	23.98	glycolaldehyde	255	
A6	24.35	glycolaldehyde	255	
A7	24.73	hydroxyacetone	269	
A8	24.93	hydroxyacetone	269	
A9	26.10	pyruvic acid or C_4 hydroxy saturated carbonyl	283	see text
A10	26.26	pentafluorobenzaldehyde	391	see text
A11	26.71	not identified		
A12	26.91	not identified		
A13	27.57	pentafluorobenzaldehyde	391	see text
A14	30.01	not identified	303	
A15	31.52	methylglyoxal	462	
A16	31.81	glyoxal	418	
A17	31.99	methylglyoxal/glyoxal	462	
A18	32.37	methylglyoxal	462/448	coelute
A19	32.55	methylglyoxal	462	
A20	33.10	2,3 butadione (biacetyl)	476	
A21	33.33	C_4 saturated dicarbonyl	476	see Table 6
A22	33.77	C_4 saturated dicarbonyl	476	see Table 6
A23	34.85	not identified	504	
A24	35.33	not identified	504	
A25	35.66	not identified	504	

TABLE 3

Carbonyl Products Detected in a Sample Collected from a Methyl Vinyl Ketone Indoor Irradiated Teflon Bag Reactor Experiment (60-m Column)

peak no.	RT	identity	MW	comment
V1	17.40	formaldehyde	225	
V2	19.51	acetaldehyde	239	
V3	19.68	acetaldehyde	239	
V4	22.62	methyl vinyl ketone	265	
V5	23.96	glycolaldehyde	255	
V6	24.30	glycolaldehyde	255	
V7	24.73	hydroxyacetone	269	
V8	24.98	hydroxyacetone	269	
V9	26.09	pyruvic acid or C_4 hydroxy saturated carbonyl	283	
V10	27.42	not identified		
V11	27.57	pentafluorobenzaldehyde	391	see text
V12	27.73	not identified		
V13	27.89	not identified		
V14	30.02	not identified	303	
V15	31.54	methylglyoxal	462	
V16	31.82	glyoxal	432	
V17	32.00	methylglyoxal/glyoxal	462/448	coelute
V18	32.37	methylglyoxal	462	
V19	32.54	methylglyoxal	462	
V20	33.11	2,3 butadione (biacetyl)	476	
V21	33.77	C_4 saturated dicarbonyl	476	see Table 6
V22	36.58	not identified	504	
V23	36.68	not identified	504	
V24	37.23	not identified	504	

observation that only a very weak peak of this compound was present in the daytime outdoor experiment sample.

Beside these identified carbonyls, there are a number of unidentified carbonyl peaks, most of whose molecular weight can be clearly determined from their CI mass spectra. These are also listed in Tables 2 and 3. Peaks A9 and V9 have a molecular weight of 283 and a base peak at $m/z = 266$ (M − 17), which indicates the presence of a hydroxy group. PFBHA will not derivatize a carbonyl functional
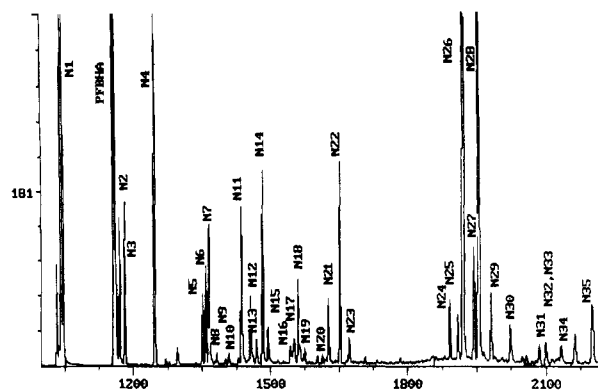

FIGURE 5. Reconstructed $m/z = 181$ ion chromatogram of a sample collected from an outdoor smog chamber isoprene/ozone nighttime experiment. Y-axis: intensity of $m/z = 181$ ion, X-axis: scan number.
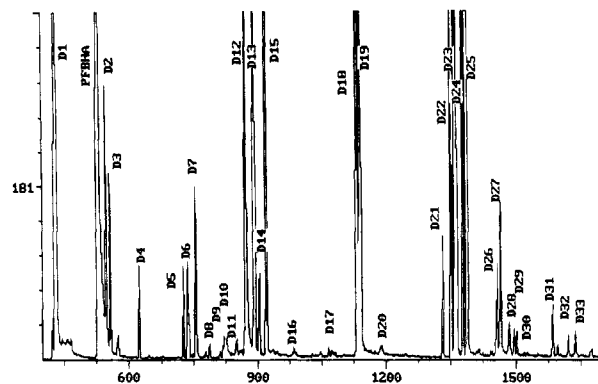

FIGURE 6. Reconstructed $m/z = 181$ ion chromatogram of a sample collected at 1005 EDT from an outdoor smog chamber isoprene/NO_x daytime experiment. Y-axis: intensity of $m/z = 181$ ion, X-axis: scan number.

group that is bonded to another oxygen, i.e., carboxylic acids and esters cannot be derivatized by PFBHA. Thus, these two peaks might be pyruvic acid or a C4 hydroxy saturated carbonyl, both having a molecular weight of 283 for their PFBHA derivative. Peaks A14 and V14 have a molecular weight of 303. In addition to the biacetyl peak in the chromatograms of both MVK and MACR, there were other peaks with the same molecular weight as biacetyl but eluting after biacetyl. The CIMS of these peaks were different than those of biacetyl. The last peaks in the chromatograms had a molecular weight of 504. We have not investigated the identity of these latter peaks. Additionally, molecular weights of peaks A11, A12, V10, V12, and V13 cannot be unambiguously determined due to possible coelution of two peaks and/or presence of unknown functional groups.

Carbonyl Analysis in Isoprene Experiments. The three isoprene indoor TBR experiments showed similar carbonyl products to those detected in the daytime outdoor chamber experiment. Therefore, only the results from the outdoor chamber experiments will be described. The reconstructed $m/z = 181$ ion chromatograms for the outdoor chamber isoprene experiments are shown in Figures 5 and 6. Because both the dark and the daylight reactions of isoprene produce methyl vinyl ketone and methacrolein, which both react with ozone and hydroxyl radicals, the chromatograms for the isoprene experiments contain not only most of the products detected in the MVK and MACR experiments but also unique compounds derived from isoprene. Tables 4 and 5 list the carbonyl products from isoprene experiments.

TABLE 4

Carbonyl Products Detected in a Sample Collected from an Isoprene/Ozone Nighttime Smog Chamber Experiment (60-m column)

peak no.	RT	identity	MW	comment
N1	17.40	formaldehyde	225	
N2	19.52	acetaldehyde	239	
N3	19.70	acetaldehyde	239	
N4	20.78	acetone	253	in distilled water
N5	22.52	methacrolein	265	
N6	22.63	methyl vinyl ketone	265	
N7	22.77	mono derivative of methylglyoxal	267	
N8	23.03	C_4 epoxy carbonyl	281	see Table 6
N9	23.48	C_4 epoxy carbonyl	281	see Table 6
N10	23.86	C_4 epoxy carbonyl	281	see Table 6
N11	23.95	glycolaldehyde	255	
N12	24.28	glycolaldehyde	255	
N13	24.36	C_4 epoxy carbonyl	281	see Table 6
N14	24.72	hydroxyacetone	269	
N15	24.93	hydroxyacetone	269	
N16	25.73	pyruvic acid or C_4 hydroxy saturated carbonyl	283	see Table 6
N17	25.85	C_4 hydroxy unsaturated carbonyl/not identified	281/295	coelute
N18	26.02	C_4 hydroxy unsaturated carbonyl	281	see Table 6
N19	26.25	pentafluorobenzaldehyde	391	see text
N20	26.71	not identified	295	
N21	27.12	C_6 unsaturated carbonyl	293	see Table 6
N22	27.53	pentafluorobenzaldehyde	391	see text
N23	27.86	not identified	317	
N24	31.53	methylglyoxal	462	
N25	31.82	glyoxal	448	
N26	32.00	methylglyoxal/glyoxal	462/448	coelute
N27	32.38	methylglyoxal	462	
N28	32.57	methylglyoxal	462	
N29	33.03	C_4 unsaturated dicarbonyl	474	see Table 6
N30	33.72	C_4 unsaturated dicarbonyl	474	see Table 6
N31	35.00	C_4 saturated dicarbonyl	476	see Table 6
N32	35.36	C_5 saturated dicarbonyl	490	see Table 6
N33	35.43	C_5 saturated dicarbonyl	490	see Table 6
N34	35.46	C_5 saturated dicarbonyl	490	see Table 6
N35	36.67	C_4 hydroxy dicarbonyl	492	see Table 6

We have demonstrated with standard samples that under certain circumstances the PFBHA derivatives of dicarbonyls will form both a mono and a di derivative. The di derivative is apparently formed stagewise, and when PFBHA reagent is not excessive, not all the mono derivatized dicarbonyls are further derivatized. The peaks N7 and D7 correspond to the mono derivative of methylglyoxal.

The peak N21 was investigated in some detail. This peak was present only in the nighttime experiment. In a second analysis on a Hewlett Packard 5890 GC connected to a VG 70-SEQ double-focusing high-resolution mass spectrometer, N21 was also detected. Two standards, acetone and methacrolein PFBHA derivatives, were measured by the VG/MS to give molecular weights of 253.0497 and 265.0509, respectively. Their precise molecular weights are 253.052605 and 265.052605 respectively, which result in a $M/\Delta M$ of 87091 and 155425. The precise molecular weight of peak N14 was 293.0865. Two formulas, $C_5H_6O_2$ and $C_6H_{10}O$, have the same nominal mass 293 for their PFBHA derivatives. A formula of $C_5H_6O_2$ has a PFBHA derivative molecular weight of 293.04752 ($M/\Delta M = 7518$), which is outside the error of the VG/MS. A formula of $C_6H_{10}O$ has a PFBHA derivative molecular weight of 293.0839 ($M/\Delta M = 112724$), which corresponds to a C_6 unsaturated aldehyde or ketone. We know from samples of background air taken from the outdoor chamber and analyzed by cryotrapping capillary column gas chromatography that no unsaturated C_6 compounds were present in the chamber before isoprene was injected.

Cremer et al. (31) suggest that a likely reaction of Criegee biradicals is an attack on a double bond or other O-acceptors. This idea was first suggested by Herron et al. (32), based on observations made by Hinrich et al. (33). Cremer et al. computed that ·CH_2OO· Criegee decomposition to give atomic oxygen is highly endothermic (73.6 kcal/mol) and that the dioxirane decomposition is even more endothermic (97.8 kcal/mol). The addition of a ·CH_2OO· Criegee biradical to an alkene however releases energy (−7.5 kcal/mol), and the epoxidation of ethene is strongly exothermic (−83 kcal/mol). These latter reactions, along with decomposition, are cited as probably the most important reactions of Criegee biradicals. The epoxidation of methacrolein and methyl vinyl ketone by ·CH_2OO· Criegee radicals gives rise to two epoxy carbonyls with a molecular weight of 281 for their PFBHA derivatives, which we observed in the isoprene nighttime experiment. The addition of ·CH_2OO· to isoprene followed by molecular decomposition results in a C_6 unsaturated carbonyl, which has the same high precision molecular weight as the N21 peak. The large concentration of isoprene and of ozone in the nighttime experiment would probably assure that one-carbon Criegee biradicals were in plentiful supply. By the time significant ozone was produced in the daylight experiment, however, all the isoprene had already been consumed. Therefore, this C_6 unsaturated carbonyl was observed in the nighttime experiment and was absent in the daytime samples.

Carbonyl Products Detected in a Sample Collected from an Isoprene/NO$_x$ Daytime Smog Chamber Experiment (30-m Column)

peak no.	RT^a	identity	MW	comment
D1	17.78	formaldehyde	225	
D2	19.58	acetaldehyde	239	
D3	19.72	acetaldehyde	239	
D4	20.75	acetone	253	in distilled water
D5	22.35	methacrolein	265	
D6	22.50	methyl vinyl ketone	265	
D7	22.79	monoderivative of methylglyoxal	267	
D8	23.30	C$_5$ unsaturated carbonyl	279	
D9	23.65	C$_5$ unsaturated carbonyl	279	
D10	23.85	glycolaldehyde	255	
D11	24.25	glycoaldehyde	255	
D12	24.56	hydroxyacetone	269	
D13	24.90	C$_4$ hydroxy unsaturated carbonyl	281	see Table 6
D14	25.05	monoderivative of C$_4$ saturated dicarbonyl	281	
D15	25.33	C$_4$ hydroxy unsaturated carbonyl	281	see Table 6
D16	26.33	C$_4$ hydroxy unsaturated carbonyl	281	see Table 6
D17	27.56	pentafluorobenzaldehyde	391	see text
D18	28.60	4-fluorobenzaldehyde	319	internal standard
D19	28.72	4-fluorobenzaldehyde	319	internal standard
D20	29.48	C$_5$ hydroxy unsaturated carbonyl	295	see Table 6
D21	29.64	methylglyoxal	462	
D22	31.95	glyoxal	448	
D23	32.08	methylglyoxal/glyoxal	462/448	coelute
D24	32.37	methylglyoxal	462	
D25	32.52	methylglyoxal	462	
D26	33.57	C$_3$ hydroxy saturated dicarbonyl	478	see Table 6
D27	33.70	C$_3$ hydroxy saturated dicarbonyl	478	see Table 6
D28	34.00	dicarbonyl	490	see Table 6
D29	34.17	dicarbonyl	490	see Table 6
D30	34.27	dicarbonyl	490	see Table 6
D31	35.55	C$_5$ unsaturated dicarbonyl	488	see Table 6
D32	36.11	C$_5$ unsaturated dicarbonyl	488	see Table 6
D33	36.35	C$_5$ unsaturated dicarbonyl	488	see Table 6

^{a} RT, corrected retention time corresponding to 60-m column, based on a linear relationship between retention times on 30-m column and those on 60-m column for known carbonyls.

To see if other ozone–alkene reactions show this reaction pathway, a TBR experiment was conducted with 1 ppm ozone and 10 ppmv 1,3-butadiene. The chromatogram of a sample collected from this experiment showed that three carbonyl peaks were present with a molecular weight of 279, which correspond to C$_5$ unsaturated carbonyls. These peaks are analogous carbonyl products to the C$_6$ unsaturated carbonyl in the isoprene–ozone reaction.

Similarly, the addition reaction of •CH$_2$OO• Cregiee biradical, either with methyl vinyl ketone or methacrolein, leads to a C$_5$ saturated dicarbonyl, which has a molecular weight of 490 for its derivative. Three peaks (N32, N33 and N34) in the nighttime isoprene–O$_3$ experiment were determined to have a molecular weight of 490.

Because OH can be produced from alkene–O$_3$ reactions, the appearance of glycolaldehyde and hydroxyacetone in the nighttime sample results from the OH oxidation of the two O$_3$–isoprene products, methacrolein and methyl vinyl ketone (3, 4, 24–36). The C$_4$ unsaturated hydroxy carbonyl and C$_4$ unsaturated dicarbonyls in the nighttime sample (peaks N17, N18, N29, and N30 in Table 4 and Figure 5) might be formed from the decomposition of Criegee biradicals. Grosjean et al. (10) suggested four pathways following rearrangement of the energetic Criegee biradicals into an energy-rich hydroxy carbonyl via a hydroxy peroxide. These were collision stabilization yielding the corresponding hydroxy carbonyl, loss of H$_2$ to produce a dicarbonyl, unimolecular decomposition leading to formation of radicals, and loss of OH. The first two pathways give rise

to a C$_4$ unsaturated hydroxy carbonyl, hydroxy methyl vinyl ketone (HOCH$_2$COCH=CH$_2$), and a C$_4$ unsaturated dicarbonyl vinyl glyoxal (HCOCOCH=CH$_2$), whose PFBHA derivatives have a molecular weight of 281 and 474. The C$_4$ unsaturated dicarbonyls appear to be unique oxidation products of isoprene in the nighttime.

A reaction scheme for the OH radical oxidation of isoprene that is consistent with our observations is given in Figure 7. The compounds enclosed in boxes in this figure were observed in our experiments. The addition of OH to isoprene followed by the addition of O$_2$ to form a peroxy radical, followed by oxidation of NO to NO$_2$ or reaction with RO$_2$ gives rise to three types of mono-hydroxy mono-unsaturated C$_5$ alkoxy radicals: β-hydroxy primary alkoxy radicals via 2-1 or 3-4 addition; β-hydroxy secondary alkoxy radicals via 4-3 addition; and β-hydroxy tertiary alkoxy radicals via 1-2 addition. There are also two pathways of OH addition that lead, via isomerization and 1-5 H-shifts, to two unsaturated C$_5$ alkoxy radicals without the hydroxy group (1-4 and 4-1 addition). Alkoxy radicals generally undergo unimolecular decomposition, react with O$_2$ via hydrogen abstraction if possible, or isomerize (38). In the case of the β-hydroxy tertiary alkoxy radicals formed via 1-2 addition, it appears from our observations that two decomposition pathways occur giving rise not only to a major product MVK but also to hydroxy-MVK (1-hydroxy-3-buten-2-one). In the case of the β-hydroxy secondary alkoxy radical from 4-3 addition, it appears that decomposition occurs to form methacrolein and that O$_2$ abstrac-
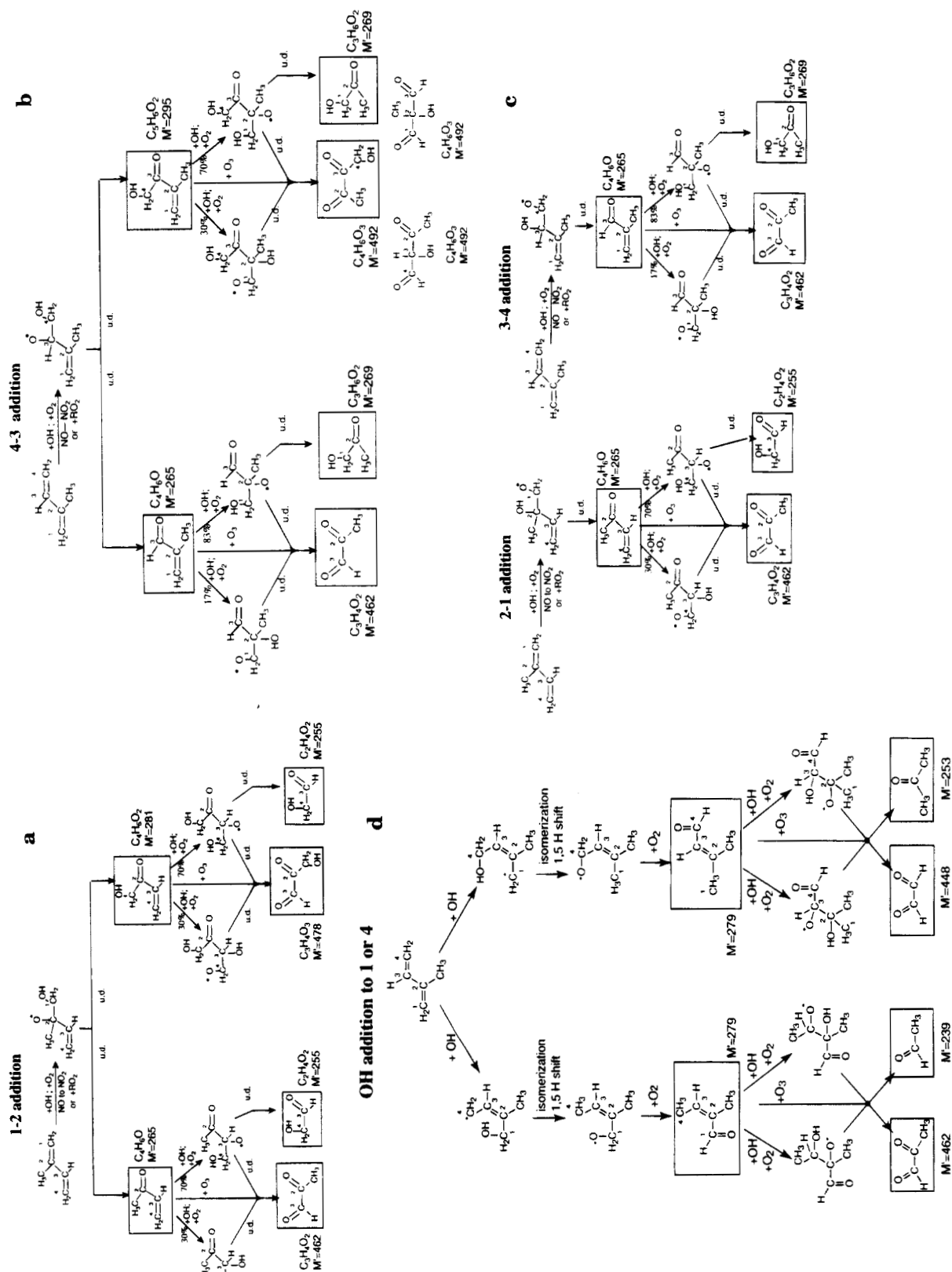
FIGURE 7. Reaction schemes for the OH radical-initiated oxidation of isoprene in the presence of NO_x. (a) 1-2 addition; (b) 4-3 addition; (c) 2-1 and 3-4 addition; (d) addition to 1 or 4 followed by isomerization.

tion (or decomposition) also occurs to form hydroxy methyl iospropenyl ketone (1-hydroxy-3-methyl-3-buten-2-one). While we observed several peaks with derivative molecular weights of 281 that also had a strong $m/z = M - 17$ ion indicative of a HO group, we observed only one peak with a derivative molecular weight of 295 corresponding to $C_5H_6O_2$ or an unsaturated C_5 hydroxy carbonyl. Paulson et al. (5) postulated the formation of six different unsaturated C_5 hydroxy carbonyls that would all have a derivative molecular weight of 295. This large variety of 295 peaks was not observed in any of our outdoor or indoor experiments with isoprene under a variety of conditions. Our observations instead suggest that unimolecular decompostion of the β-hydroxy primary alkoxy radicals is much faster than oxygen abstraction of hydrogen and that in these cases the corresponding postulated unsaturated C_5 hydroxy carbonyls would not be formed.

We also observed methylglyoxal, glycolaldehyde, and hydroxyacetone, and these are major products from the OH and O_3 oxidation of methacrolein and methyl vinyl ketone as was demonstrated in the TBR experiments. Two peaks, D26 and D27, were found to have a derivative molecular weight of 478, corresponding to a C_3 hydroxy dicarbonyl such as hydroxy methylglyoxal as shown in the 1-2 addition pathway of Figure 7. The observation of hydroxy methyglyoxal is therefore consistent with the formation of HO-MVK. Similarly, in the isoprene TBR experiments, a peak was observed which had a derivative molecular weight of 492, corresponding to a C_4 hydroxy dicarbonyl such as hydroxy biacetyl. Unfortunately, in the daytime isoprene experiments, the GC analysis was not allowed to proceed long enough to have observed this compound, which has a long retention time. The presence of hydroxy biacetyl is consistent with the reaction of hydroxy methyl isopropenyl ketone as shown in the 4-3 addition pathway of Figure 7.

We observed two peaks, D8 and D9, that have a derivative molecular weight that corresponds to a C_5 unsaturated carbonyl (279). Such compounds might form by a 1 or 4 addition of OH to isoprene followed by a 1-5 hydrogen shift and subsequent abstraction of a terminal hydrogen by oxygen to produce either 2-methyl-2-butenal or 3-methyl-2-butenal (see 1 or 4 OH addition pathways in Figure 7). Paulson et al. (2) also reported the identification of 2-methyl-2-butenal in their outdoor smog chamber experiments. Reactions of methyl-2-butenals, either with ozone or with OH radicals would lead to methylglyoxal, glyoxal, acetone, and acetaldehyde, and all of these were observed.

The D31, D32, and D33 peaks have molecular weights that correspond to C_5 unsaturated dicarbonyls. A possible formation pathway is the OH oxidation of 3-methylfuran, which was reported to have a yield of 0.044 from the reaction of OH with isoprene (3, 37). Our studies show that the gas-phase OH oxidation of furan and 2.5-dimethylfuran gives major products butendial and 3-hexen-2,5-dione, respectively. Similarly, OH oxidation of 3-methylfuran leads to 2-methylbutendial, which has a molecular weight of 488 for its PFBHA derivative.

Previous studies on isoprene oxidation products have shown that the identified products failed to account for all the reacted isoprene. Our carbonyl analysis of isoprene samples clearly suggests that at least a fraction of the missing isoprene is in the form of a number of multi-functional

carbonyls such as hydroxy carbonyls, dicarbonyls, and hydroxy dicarbonyls, which agrees with the observation by Tuazon and Atkinson (2). They observed that there were unidentified carbonyls by using FTIR spectrometer to monitor the products from an irradiated isoprene–NO_x mixture. As suggested by our results, Tuazon and Atkinson's missing reacted carbon probably exists as a number of different compounds with small yields, making their identification difficult.

We have shown that by using PFBHA-GC/MS/IT, the molecular weight and class can be determined for these otherwise unidentified carbonyls. These additional data narrow the possibilities to a limited number of species, thus offering guidance in producing an authentic standard. Possible structures consistent with the molecular weights of most of the unidentified carbonyls we detected are given in Table 6. Most of these carbonyls are not commercially available. Synthesis of these compounds in the laboratory is necessary to further prove their identities. We are in the process of performing such synthesis for the most likely compounds listed in Table 6, and we will report this work in a future article.

Quantitative analysis is possible for carbonyls that have standards available. Our preliminary work and other researchers' work (21, 22) have demonstrated that carbonyls in water in the low ppb range can be detected using GC/MS under selected ion monitoring (SIM) mode. If we assume a 100% collection efficiency of airborne carbonyls and a collection volume of 10 L of air, 1 ppb detected in water corresponds to 1 ppbV in the gas phase for a carbonyl with a molecular weight of 100. At a sampling rate of 0.5 L/min, a time resolution of 20 min can be achieved to detect carbonyls of concentrations at as low as several ppbV. We are working on improving the collection efficiency of

TABLE 6
Possible Structure of Unidentified Carbonyls Consistent with the Molecular Weights Listed in Tables 4 and 5

Sample	peak	M.W.	Possible Structures
day	D8, D9	279	(structures for 279)
day, night	D13, D14, D15, D16, N8, N9, N10, N13, N18	281	(structures for 281)
night	N22	293	(structures for 293)
day	D20	295	(structure for 295)
night	N29, N30	474	(structure for 474)
night	N31, A21, A22, V21	476	(structures for 476)
night (s) day(w)	N35	492	(structure for 492)
day goes away	D26, D27	478	(structure for 478)
day goes away	D31, D32, D33	488	(structure for 488)
day grows	D23, D24, D25, N32, N33, N34	490	(structures for 490) and other isomers

airborne carbonyls and will present quantitative results in the near future.

Conclusion

We have demonstrated that the PFBHA derivatives of airborne carbonyls can be analyzed by GC/MS/IT. The strong ion at $m/z = 181$ is a convenient indicator of the presence of carbonyl compounds. Both EI and CI spectra offer molecular weight information of the carbonyl compounds. CI spectra provides unambiguous molecular weight diagnosis for all the carbonyls examined by showing strong signals of ions characteristic of molecular weight. The examples show that unidentified multi-functional carbonyls contribute to a fraction of the missing carbons in the atmospheric oxidation of isoprene. The absence of multiple unsaturated C_5 hydroxy carbonyls, however, does not support previously proposed reaction mechanisms in which these compounds had a major role (5). Evidence was found to support the formation of a C_4 unsaturated hydroxy carbonyl, hydroxy methyl vinyl ketone, and a C_5 unsaturated hydroxy carbonyl, hydroxy methyl isopropenyl ketone. There is also evidence that under high concentrations of ozone and isoprene conditions, $\cdot CH_2OO\cdot$ Crigee biradicals add to isoprene forming a C_6 unsaturated carbonyl. Such reactions are not expected to be important in ambient air.

This method is superior to the frequently used DNPH method in that it is able to determine α-hydroxy carbonyls and α-dicarbonyls, and it has better resolution for similar carbonyls. A significant difference is that the use of GC/MS/IT analysis of these derivatives also allows determination of the molecular weights of unknown carbonyls.

Acknowledgments

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