

Development of a Compound-Specific Isotope Analysis Method for Atmospheric Formaldehyde and Acetaldehyde

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A novel method determining compound-specific carbon isotopic compositions for atmospheric formaldehyde and acetaldehyde in ppb or sub-ppb levels by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) is presented. Atmospheric carbonyls are collected using the conventional 2,4-dinitrophenylhydrazine (DNPH) derivatization method, and their $\delta^{13}\text{C}$ values are calculated based on stoichiometric mass balance after measuring the carbon isotopic compositions of the carbonyl–DNPH derivatives and DNPH, respectively. Using formaldehyde, acetaldehyde, and DNPH standards with their $\delta^{13}\text{C}$ values predetermined, the $\delta^{13}\text{C}$ fractionation is evaluated for derivatization processes both in solutions and in simulation experiment of atmospheric sampling. In these two derivatization systems, through reduplicate $\delta^{13}\text{C}$ analysis, good reproducibility of the derivatization process is found with an average error of less than 0.5‰, and the differences between the predicted and the measured $\delta^{13}\text{C}$ values range from -0.18 to 0.49 ‰, indicating that the derivatization process introduces no isotopic fractionation for both formaldehyde and acetaldehyde. Thus, the $\delta^{13}\text{C}$ values of the original underivatized carbonyls can be accurately calculated through mass balance equation. Using the method developed, preliminary tests of atmospheric formaldehyde and acetaldehyde at two urban sites were conducted and revealed significant differences of their isotopic compositions, implying possible application of the method in helping us understand the primary emission, secondary formation, or removal processes of carbonyls in the atmosphere.

Introduction

As key participants in photochemical reactions influencing smog processes in the atmosphere, carbonyl compounds have been paid increasing attention recently (1, 2), especially

for formaldehyde and acetaldehyde, the most abundant carbonyl compounds. The carbonyl compounds offer important mechanistic insights into the oxidation processes (3–5) and play a crucial role in the formation of photooxidants such as ozone and OH radicals (6).

Carbonyl compounds can be emitted directly from auto exhausts, industrial emissions, and biogenic emissions of some plants and can be also produced in situ by photooxidation of both anthropogenic and biogenic hydrocarbons (e.g., isoprene) in the atmosphere (4, 7). Thus, the carbonyls are both primary (directly emitted) and secondary (formed in the atmosphere) (8), resulting in the complicated source identification for carbonyl compounds.

Recently, studies of isotope compositions of trace atmospheric species (e.g., CO_2 , CH_4 , and nonmethane hydrocarbons) have provided valuable information about the transition mechanism and source identification (9, 10). However, there are very few studies on the carbon isotopes of atmospheric carbonyls (11, 12). Johnson and Dawson (12) developed a method to collect the atmospheric formaldehyde and obtained preliminary $\delta^{13}\text{C}$ data at two remote sampling sites. From then on, there are no further studies on this field.

In this paper, a novel procedure was developed to determine the carbon isotopic compositions of atmospheric formaldehyde and acetaldehyde. DNPH derivatization is a necessary step for the collection and measurement of atmospheric carbonyls in many recent studies (13–16). The derivatization process introduces additional carbon atoms, and consequently, alteration of the original carbon isotopic composition of the carbonyls occurs. It is imperative that we develop an understanding of the relationship between the $\delta^{13}\text{C}$ of carbonyl derivatives and the $\delta^{13}\text{C}$ of the underivatized carbonyls. In the present study, formaldehyde and acetaldehyde standards were used to test $\delta^{13}\text{C}$ relationship and fractionation during the derivatization with DNPH of a known stable carbon isotope composition both in solutions and in simulation experiments of atmospheric sampling. The results of GC/C/IRMS analysis of carbonyls at two sampling sites are also presented.

Experimental Procedures

Chemicals and Materials. All solvents employed were HPLC grade. Water was double distilled and filtrated by Milli-Q. Acetonitrile (ACN) was purchased from Merck (Germany). The sampling medium was a Sep-Pak Silica Gel Cartridge (Waters, Millipore Corp). DNPH (99%) was purchased from Fluka (Germany) and was purified by recrystallization 3 times from HPLC grade ACN. DNPH of the same lot number was used for all derivatizations and the collection of atmospheric carbonyls.

Formaldehyde and acetaldehyde from four suppliers were used. Formaldehyde (37% in water solution with 10% methanol) was supplied by Guangzhou Chemical Reagents (China) (M1), Aldrich (M2), Guangzhou Donghong Chemicals (China) (M3), and Guangzhou Second Chemicals (China) (M4), respectively. Acetaldehyde (40% purity) was supplied by Tianjin Kemiou Chemical Reagents (China) (M5) and Shanghai Medical Reagents (China) (M8), and acetaldehyde (99.5% purity) was supplied by Dr. Ehrenstorfer GmbH (Germany) (M6) and Aldrich (M7), respectively.

Synthesis of the Pure Carbonyl–DNPH Derivatives. A saturated DNPH solution was prepared by adding enough purified DNPH to about 100 mL of 2 N HCl solution, and it was then filtered through filter paper after heating and dissolution. Then in the filtrate, the DNPH derivatives were synthesized by reacting DNPH with excess formaldehyde

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and acetaldehyde, respectively. The carbonyl–DNPH derivative was washed with water and methanol, then recrystallized 2 times using methanol. After that, the quality and purity of the crystals were validated by HPLC and then stored in a refrigerator. These derivatives were used as the standards to qualify the compounds during the GC/C/IRMS analysis of atmospheric samples.

Liquid Derivatization between DNPH and Carbonyls.

The DNPH derivatives were prepared by reacting corresponding carbonyl compounds (formaldehyde and acetaldehyde) with excess DNPH in ACN solutions; some orthophosphoric acid was added as the catalyst. The carbonyl–DNPH derivative solutions (still containing unreacted DNPH) were subjected to GC/C/IRMS analysis.

Simulation Experiment of Atmospheric Sampling.

The experiments were performed using a self-made system. The system included a 15 L stainless chamber, with a recycling pump installed between inlet and outlet ports connected by the Teflon tubes. Before every simulation experiment, the chamber was flushed by high purity N₂ (99.99%) at least 10 times. After the chamber was filled with N₂, the carbonyl solution (its carbonyl $\delta^{13}\text{C}$ value was predetermined by GC/C/IRMS) was injected into the chamber and heated to enable it to evaporate. The N₂ (containing carbonyls) was cycled by the pump for about 30 min, and then the carbonyl was collected by drawing the gas with the recycling pump through a sampling cartridge (detailed description as follows) connected between the two ports. After sampling for 30 min, the cartridge was removed, and the corresponding carbonyl–DNPH derivatives were washed out with 1 mL of ACN. Then, the solutions were blown by gentle N₂ flow to about 0.1 mL (just as the procedure conducted after the atmospheric sampling). Finally, the samples were injected to GC/C/IRMS for carbon isotope analysis.

Carbonyl Sampling. The whole method was described in the previous study (15). The sampling medium was a Sep-Pak Silica Gel Cartridge (Waters, Millipore Corp). Each cartridge was rinsed by attaching a syringe filled with 10 mL of ACN and then coated slowly by passing 7 mL of the freshly made coating solution, which contained 60 mL of DNPH–ACN-saturated solution and 4 mL of concentrated orthophosphoric acid in 500 mL of ACN, through the cartridge by gravity. When there was no more solution flowing out of the cartridge, the cartridge was dried with a gentle flow of nitrogen for 15 min and then wrapped in aluminum foil, sealed in Teflon bags, and stored in a refrigerator at 4 °C until use. Three blank cartridges from each cartridge batch were analyzed, and the results were below the EPA blank criteria (formaldehyde concentration <0.15 $\mu\text{g}/\text{cartridge}$ and acetaldehyde concentration <0.1 $\mu\text{g}/\text{cartridge}$; both were less than 5% of the concentrations for the corresponding analyte from an air sample when the carbonyl (e.g., formaldehyde) was collected as a DNPH derivative).

Samples were collected by drawing the air with a sampling pump (Thomas) through the cartridge. A potassium iodide (KI) denuder was connected to the upstream of the cartridge to prevent the interference of ozone (16). After sampling, each cartridge was wrapped in aluminum foil, resealed with a Teflon bag, and transported back to the laboratory and stored in the refrigerator before being analyzed. Each sampling program included one laboratory blank and one field blank, and at each sampling site, two field samples were collocated with a back-up cartridge to evaluate the breakthrough (second elution tests indicated the recovery of more than 95% for formaldehyde and acetaldehyde).

The typical sampling flow rate was 2 L/min, and the sampling duration was 20–24 h. After sampling, a sampled cartridge was eluted with 1 mL of acetonitrile and the solution was blown by the gentle flow of nitrogen to about 0.1 mL before analysis.

Analytical Procedure. Two kinds of GC/C/IRMS systems were used in our study on compound-specific carbon isotope ratios analysis. The analysis of carbonyl DNPH derivatives was performed using an HP 6890 GC (Agilent) column combined with a Finnigan DELTA^{plus}XL mass spectrometer. The injector was set at 290 °C, the amount of carbonyl derivatives in each injection (sample size of about 1 μL) was over 200 ng, and a splitless model was used. For the analysis of derivatives prepared in the laboratory, the GC was equipped with a DB-5 column (30 m \times 0.32 mm \times 0.25 μm , J&W Scientific), and the following oven temperature program was used: 180 °C at the start, 3 °C/min to 250 °C, and then 20 °C/min to 290 °C. For the analysis of environmental samples, the GC was equipped with a DB-5 column (50 m \times 0.32 mm \times 0.25 μm , J&W Scientific), and the oven temperature program was set 60 °C at the start, 20 °C/min to 200 °C, 3 °C/min to 250 °C, 20 °C/min to 290 °C, and 290 °C for 5 min. Helium was used as the carrier gas at 1 mL/min. The combustion interface was operated at 980 °C; reoxidation was performed once a day for ca. 30 min. The mass spectrometer provided real-time measurements of the $^{13}\text{C}/^{12}\text{C}$ ratios for each CO₂ peak. An external CO₂ reference gas ($\delta^{13}\text{C} = -29.10\text{‰}$) was used to obtain highly accurate isotopic compositions. The reproducibility and accuracy of carbon isotopic analyses were evaluated routinely every day using 10 laboratory isotopic standards (C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₂, C₂₅, C₂₈, C₃₀, and C₃₂ *n*-alkanes supplied by Indiana University) with predetermined isotopic values (–31.89, –30.67, –30.53, –31.02, –32.24, –32.77, –28.49, –32.11, –33.05, and –29.41‰, respectively) (17). For the analysis of laboratory isotopic standards, the GC was run in a split ratio of 5:1 using the same parameter except for the temperature program: 80 °C at the start, 10 °C/min to 290 °C, and 290 °C for 30 min. However, for $\delta^{13}\text{C}$ analysis of underivatized carbonyls, the HP 5890 GC combined with an Isochrom II isotope ratio mass spectrometer was used (18). The GC was run in a split ratio of about 10:1, and the injector was set at 100 °C. An HP-PLOT Q column (30 m \times 0.32 mm \times 20 μm , Hewlett-Packard) was used, and the oven temperature was kept at 180 °C. The temperature at the combustion was 850 °C, and CO₂ of known isotopic composition was used as the reference gas. CH₄ of a known $\delta^{13}\text{C}$ value (–36.30‰) was used as the laboratory isotopic standard to check the reproducibility and accuracy of the carbon isotopic analysis routinely. For both analysis systems, the sextuple analysis of laboratory isotopic standards indicated excellent accuracy and reproducibility of carbon isotopic analysis (the corresponding standard deviation ranged from 0.17 to 0.32‰, and the deviation between the measured data and the predetermined data ranged from –0.07 to 0.25‰).

Elemental analyzer–isotope ratio mass spectrometry (EA/IRMS) was performed as follows: samples were put into cleaned tin capsules and weighed. Capsules containing weighed samples were placed in the CE EA1112 C/N/S analyzer and burned at 960 °C in an O₂ atmosphere in a combustion tube. Combustion gases were swept through a reduction column by a stream of inert He gas and passed into a gas chromatography where CO₂, still in the He stream, was separated from other gases. The gas stream then entered a DELTA^{plus}XL mass spectrometer where the CO₂ gas was analyzed and compared to the reference CO₂ gas of known $\delta^{13}\text{C}$ value (–29.10‰, calibrated against the NBS-22 reference material with $\delta^{13}\text{C}$ value –29.7‰) (19). During every batch of analyses, an empty tin capsule was analyzed as the blank to check the background, and the carbon black sample of known $\delta^{13}\text{C}$ value (–36.91‰) was used to check the reproducibility and accuracy. Low background (peak height <0.02 V, much lower than the peak height of the sample, greater than 1.5 V), excellent reproducibility, and accuracy were achieved; the corresponding standard deviation of

TABLE 1. Stable Carbon Isotopic Compositions of Measured and Predicted Carbonyl–DNPH Derivatives in Liquid Derivatization

carbonyl	suppliers	$\delta^{13}\text{C}$			Δ^f
		underivatized carbonyl ^{a,b}	measured carbonyl–DNPH derivatives ^{a,b,c}	predicted carbonyl–DNPH derivatives ^{a,c,d}	
formaldehyde	M1	-39.30 ± 0.31 <i>n</i> = 5	-28.82 ± 0.10 <i>n</i> = 9 ^e	-28.79	0.03
	M2	-45.08 ± 0.40 <i>n</i> = 5	-29.83 ± 0.19 <i>n</i> = 9	-29.62	0.21
	M3	-38.08 ± 0.23 <i>n</i> = 5	-28.62 ± 0.23 <i>n</i> = 9	-28.62	0.0
acetaldehyde	M5	-27.27 ± 0.29 <i>n</i> = 5	-27.26 ± 0.12 <i>n</i> = 9	-27.10	0.16
	M6	-30.41 ± 0.44 <i>n</i> = 5	-27.82 ± 0.12 <i>n</i> = 9	-27.88	-0.06
	M7	-26.35 ± 0.20 <i>n</i> = 5	-27.12 ± 0.09 <i>n</i> = 9	-26.87	0.25

^a Stable carbon isotopic compositions reported in per mil relative to PDB. ^b $\delta^{13}\text{C}$ determined by GC/C/IRMS analysis. ^c $\delta^{13}\text{C}_{\text{DNPH}} = -27.04 \pm 0.26$ ‰, from 14 analyses determined by EA/IRMS. ^d On the basis of mass balance relationship eq 1 of carbonyls' $\delta^{13}\text{C}$ determined by GC/C/IRMS and DNPH's $\delta^{13}\text{C}$ determined by EA/IRMS. ^e Values represent means and standard deviations for three separate derivatization samples (and three analyses for each sample). ^f Predicted $\delta^{13}\text{C}$ – measured $\delta^{13}\text{C}$. *n*: number of times repeated during the GC/C/IRMS analysis.

TABLE 2. Stable Carbon Isotopic Compositions of Measured and Predicted Carbonyl–DNPH Derivatives in Simulation Experiments of Atmospheric Sampling

carbonyl	suppliers	aldehyde concentrations (ppm)	$\delta^{13}\text{C}$			Δ^e
			underivatized carbonyl ^{a,b}	measured carbonyl–DNPH derivatives ^{a–c}	predicted carbonyl–DNPH derivatives ^{a,c,d}	
formaldehyde	M2	1.27	-45.08 ± 0.40 ; <i>n</i> = 5	-29.44 ± 0.28 ; <i>n</i> = 4	-29.62	-0.18
		1.9		-29.98 ± 0.05 ; <i>n</i> = 3		0.36
	M4	1.9	-42.11 ± 0.13 ; <i>n</i> = 3	-29.14 ± 0.37 ; <i>n</i> = 4	-29.19	-0.05
acetaldehyde	M5	3.2		-29.11 ± 0.13 ; <i>n</i> = 3		-0.08
		0.64	-27.27 ± 0.29 ; <i>n</i> = 5	-27.59 ± 0.22 ; <i>n</i> = 3	-27.10	0.49
	M8	1.9	-27.38 ± 0.23 ; <i>n</i> = 3	27.57 ± 0.09 ; <i>n</i> = 3	-27.13	0.47
		1.9		-27.24 ± 0.25 ; <i>n</i> = 3		0.11
				-27.39 ± 0.16 ; <i>n</i> = 3		0.26

^a Stable carbon isotopic compositions reported in per mil relative to PDB. ^b $\delta^{13}\text{C}$ determined by GC/C/IRMS analysis. ^c $\delta^{13}\text{C}_{\text{DNPH}} = -27.04 \pm 0.26$ ‰, from 14 analyses determined by EA/IRMS. ^d On the basis of mass balance relationship eq 1 of carbonyls' $\delta^{13}\text{C}$ determined by GC/C/IRMS and DNPH's $\delta^{13}\text{C}$ determined by EA/IRMS. ^e Predicted $\delta^{13}\text{C}$ – measured $\delta^{13}\text{C}$. *n*: number of times repeated during the GC/C/IRMS analysis.

analysis and the deviation between the measured data and the predetermined data were less than 0.3‰.

All $^{13}\text{C}/^{12}\text{C}$ ratios are expressed in conventional delta (δ) notation, which is the per mil (‰) deviation from the standard Pee Dee Belemnite (PDB).

Measurement of $\delta^{13}\text{C}$ Values of Standard Materials. The $\delta^{13}\text{C}$ values of DNPH reagent and the derivatives used in this study were determined using the EA/IRMS system and the GC/C/IRMS instrument, respectively. For underivatized formaldehyde and acetaldehyde, the $\delta^{13}\text{C}$ values were determined by GC/C/IRMS instrument as follows: about 1 mL solution of formaldehyde (acetaldehyde) was sealed in a 2 mL glass bottle with an open screw cap containing a Teflon lined silica septum; after allowing at least 1 h for equilibrium, gas samples (about 1 mL) containing enough amount of aldehyde from the glass bottles were injected into the split/splitless injection port of the GC using a Hamilton gastight locking syringe, and the carbon isotope analysis was performed as described previously. Other components (e.g., methanol in formaldehyde water solutions) were in good separation with target compounds.

Results and Discussion

$\delta^{13}\text{C}$ Analysis of Carbonyls and Derivatives Prepared through Liquid Derivatization. In liquid derivatization, the preparation of carbonyl DNPH derivatives alters the original stable isotope compositions of the carbonyls. To correct for

the introduction of carbon during derivatization, it is necessary to assess the isotopic reproducibility of the derivatization method. The $\delta^{13}\text{C}$ values of formaldehyde (acetaldehyde) samples from three different suppliers, and their respective DNPH derivatives, were determined by GC/C/IRMS and are presented in Table 1. In general, the derivatization of three respective samples of each carbonyl from a given supplier was accomplished with a reproducibility (1 standard deviation) of less than 0.3‰ (ranged from 0.09 to 0.23‰). The analytical error obtained for three GC/C/IRMS analyses of carbonyl DNPH derivatives of the same sample ranged from 0.06 to 0.48‰ and averaged 0.24 ± 0.15 ‰. The analytical error obtained for five GC/C/IRMS analyses of underivatized carbonyl of the same sample ranged from 0.15 to 0.44‰, averaged 0.28 ± 0.10 ‰. These reproducibilities compare well with those obtained in the derivatization of fatty acids (20) and are within the error reported for GC/C/IRMS $\delta^{13}\text{C}$ determinations of compounds that do not require derivatization prior to analysis (9, 10).

$\delta^{13}\text{C}$ Analysis during the Simulation Experiment of Atmospheric Sampling. Also in the simulation experiment, the $\delta^{13}\text{C}$ values of formaldehyde (acetaldehyde) from two different suppliers, and their respective DNPH derivatives (collected by a sampling cartridge), were determined by GC/C/IRMS and are presented in Table 2. Although the carbonyls of different concentrations were collected, the derivatization of two respective samples of each carbonyl

TABLE 3. Stable Carbon Isotopic Compositions of Formaldehyde and Acetaldehyde at Two Urban Sites

sampling site	sampling date	formaldehyde concentrations ^a (μg/m ³)	acetaldehyde concentrations ^a (μg/m ³)	measured formaldehyde derivatives ^{b-e}	δ ¹³ C		
					calculated underivatized formaldehyde ^{b,e-g}	measured acetaldehyde derivative ^{b-e}	calculated underivatized acetaldehyde ^{b,e-g}
S1 ^h	03-7-9	14.07 ± 3.11	7.38 ± 2.12	-26.99 ± 0.22	-26.69 ± 2.19	-27.58 ± 0.21	-29.2 ± 1.32
	03-7-10			-27.25 ± 0.11	-28.51 ± 1.74	-27.60 ± 0.33	-29.28 ± 1.53
S2	03-6-13	66.97 ± 14	23.15 ± 3.38	-25.56 ± 0.16	-16.68 ± 1.92	-25.53 ± 0.26	-21.00 ± 1.30
	03-6-14			-25.89 ± 0.16	-18.99 ± 1.92	-25.53 ± 0.08	-21.00 ± 0.84

^a The concentrations; see ref 23. ^b Stable carbon isotopic compositions reported in per mil relative to PDB. ^c δ¹³C determined by GC/C/IRMS analysis. ^d Values represent means and standard deviations for three analyses. ^e δ¹³C_{DNPH} = -27.04 ± 0.26 ‰, from 14 analyses determined by EA/IRMS. ^f On the basis of mass balance relationship eq 1 of carbonyl DNPH derivatives' δ¹³C determined by GC/C/IRMS and DNPH's δ¹³C determined by EA/IRMS. ^g Standard deviation was calculated according to eq 2. ^h S1: petrochemical refinery. S2: bus station.

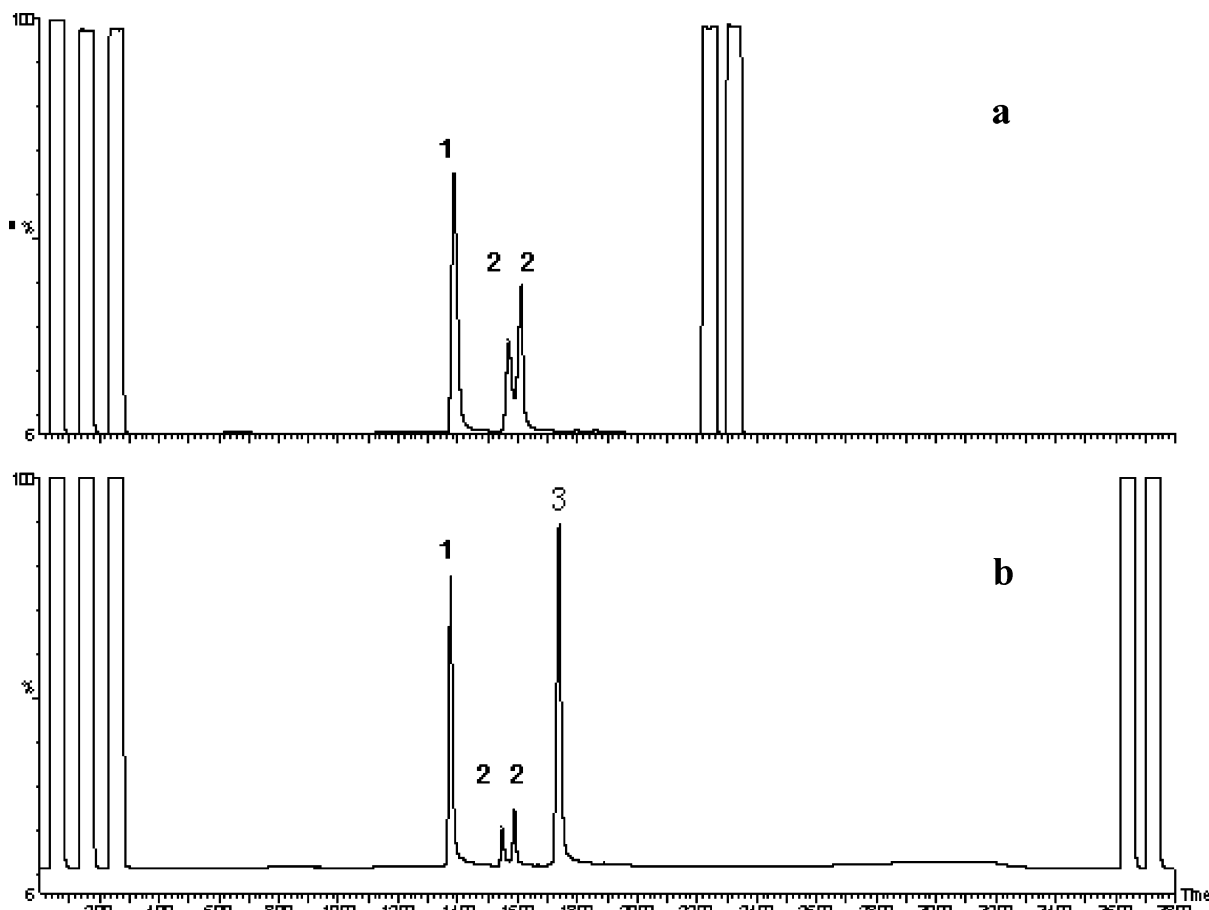


FIGURE 1. Typical GC/C/IRMS chromatogram of carbonyl-DNPH derivatives. (a) Authentic standard and (b) sample collected at a petrochemical refinery in Guangzhou, July 10, 2003. 1: Formaldehyde-DNPH derivative; 2: acetaldehyde-DNPH derivative; and 3: acetone-DNPH derivative.

from a given supplier was accomplished well with a reproducibility (1 standard deviation) of less than 0.5‰ (ranged from 0.01 to 0.38‰). The analytical error obtained for three or four GC/C/IRMS analyses of carbonyl DNPH derivatives of the same sample ranged from 0.05 to 0.37‰ and averaged 0.19 ± 0.11‰. The analytical error obtained for three or five GC/C/IRMS analyses of underivatized carbonyl of the same sample ranged from 0.13 to 0.40‰, averaged 0.26 ± 0.11‰. The reproducibility was also excellent as compared to that of the previous studies.

Isotopic Fractionation during Derivatization. Theoretically, the carbonyl DNPH derivatives should exhibit δ¹³C compositions that reflect the relative contributions of carbon from each component and their respective δ¹³C values. If there is no isotopic fractionation during the carbonyl

derivatization reaction, the generalized stoichiometric mass balance equation for carbonyl and their derivatives may be written as

$$\delta^{13}\text{C}_{\text{derivatives}} = f_{\text{carbonyl}} \delta^{13}\text{C}_{\text{carbonyl}} + f_{\text{DNPH}} \delta^{13}\text{C}_{\text{DNPH}} \quad (1)$$

where f_{carbonyl} and f_{DNPH} are the mole fractions of carbon in the carbonyl DNPH derivatives arising from the underivatized carbonyl and DNPH reagent, respectively. For example, f_{carbonyl} has the value of 1/4 for the derivatization of acetaldehyde. This equation can be used to estimate the carbon isotope composition of the original carbonyl (δ¹³C_{carbonyl}) from the known isotope composition of DNPH (δ¹³C_{DNPH}) and the measured isotope composition of carbonyl DNPH derivatives (δ¹³C_{derivatives}). It should be pointed out that the analytical

error of the calculated data for underivatized carbonyl (usually expressed as the standard deviation, S) could be calculated by the following equation (concluded from eq 1):

$$S^2_{\text{carbonyl}} = 1/f^2_{\text{carbonyl}} S^2_{\text{derivatives}} + (f_{\text{DNPH}}/f_{\text{carbonyl}})^2 S^2_{\text{DNPH}} \quad (2)$$

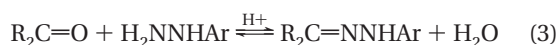
f_{carbonyl} and f_{DNPH} are the same as in eq 1, and $S_{\text{derivatives}}$ and S_{DNPH} are the standard deviation (S) of the measured carbon isotope data of carbonyl DNPH derivatives and DNPH, respectively. From eq 2, it is known that for the relatively light aldehyde (with small mole fractions of carbon in the carbonyl DNPH derivatives), the analytical error would be larger than those of the heavier ones (see Table 3).

Tables 1 and 2 compare the $\delta^{13}\text{C}$ values predicted by eq 1 to those measured by GC/C/IRMS. The predicted and measured values agreed within the precision limits of the GC/C/IRMS measurements (ranging from -0.18 to 0.49). Also note that the calculated isotopic difference between predicted and measured values can be ignored.

During the derivatization processes, fractionations are generally caused by kinetic isotope effects. Rieley (21) has described several possible kinetic isotope effects. The primary isotope effect, whereby a bond containing the atom under consideration is changed in the rate-determining step, is the most significant (22). If no carbon bond is changed in the rate-determining step, and indeed if no carbon-containing bond is involved in the reaction, then there is not likely to be a primary isotope effect on $\delta^{13}\text{C}$.

If a kinetic isotope effect is to cause an isotope fractionation at a specific carbon position, there must be incomplete conversion of reactant containing the carbon bond involved in the rate-determining step (nonquantitative reaction). In derivatization reactions, the most likely effect will come from a nonquantitative reaction of one of the reagents, allowing for a kinetic isotope effect to be expressed at any carbon center involved in the rate-determining step and causing a fractionation of carbon isotopes at a specific position in the derivatized compound. If the reagent containing the carbon bond altered in the rate-determining step is in excess relative to other reagents, then full expression of the kinetic isotope effect would be expected. However, if all the reagents containing the carbon bond altered in the rate-determining step are to react to form the derivative (quantitative reaction), then no fractionation would be expected.

In the present study on carbonyl DNPH derivatization, the carbonyls react with DNPH as follows:



where $\text{R} = \text{CH}_3$ or H and $\text{Ar} = 2,4\text{-dinitrophenyl}$. It is clear that only carbonyl contributes a carbon atom whose bonding is altered in the rate-determining step (the reaction position of DNPH is the nitrogen atom); then the carbon kinetic isotope effect is mostly related to the carbonyl. However, in the liquid derivatization, the simulation experiment and the air sampling conditions, the DNPH reagent is always used in excess. Although the carbonyl has a carbon bond altered in the rate-determining step, it reacts quantitatively and thus introduces no effect on carbon isotope fractionation. Thus, it is predicted that no carbon isotope fractionation should occur during the synthesis of DNPH derivatives in our study conditions, which is confirmed by the present study.

Measurements of Atmospheric Samples. Samples were taken at two locations: a petrochemical refinery and a bus station in Guangzhou, Guangdong Province, China. The description of sampling sites was as follows (23):

(S1) an industrial area near a petrochemical factory in the Huangpu District. The sampling site was on the top of a two-floor building 5 m high above ground level and

(S2) a bus station near the Guangzhou East Railway Station in the Tianhe District, which corresponded to an area of ca. 17 300 m², with a roof and eight exits and eight carriage drives. The predominant traffic was gasoline-fueled heavy-duty buses and only a small proportion of diesel-fueled buses. The bus station could raise the rate to 4500 bus/day. It was not only a parking place, but the buses came and went frequently, and there were also many passengers waiting for the buses.

The target compounds in samples were in good separation (Figure 1), while the acetaldehyde DNPH derivative gave rise to obvious double peaks, due to the formation of both E and Z isomers during the reaction in acidic medium (24). The $\delta^{13}\text{C}$ values of the acetaldehyde DNPH derivative were obtained by defining these two peaks as one using the integral tools of IRMS software. ^{13}C data of the target compounds are shown in Table 3. It could be seen that the data of atmospheric formaldehyde and acetaldehyde were distinctly different, which might reflect different sources of formaldehyde and acetaldehyde (e.g., methane and NMHC, the precursors of carbonyl). For petroleum sources, the ^{13}C compositions of C1–C4 alkanes are generally intermediate between -80 and -40‰ (25); however, for engine exhaust and fuel losses, the ^{13}C compositions of alkanes and alkenes are about -27‰ (9). Both of our values are much heavier (more enriched in ^{13}C) than those of possible precursors. This may be the result of isotopic fractionation induced by solar photolysis (11, 12) or other reasons. Further work on this field is needed.

Acknowledgments

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Supporting Information Available

Our real measurements of reference materials such as Indiana's *n*-alkanes (Table 1), carbon black and the CH₄ standards (Table 2), and the comparison of the $\delta^{13}\text{C}$ data of the reference *n*-alkanes between two GC/C/IRMSs (DELTA^{plus} XL and Isochrom) (Table 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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