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Stable carbon isotope composition of secondary organic aerosol from β-pinene oxidation

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[1] A chamber study was carried out to investigate the stable carbon isotopic composition (δ^{13}C) of secondary organic aerosol (SOA) formed from ozonolysis of β-pinene. β-Pinene (600 ppb) with a known δ^{13}C value (-30.1‰) and 500 ppb ozone were injected into the chamber in the absence of light and the resulting SOA was collected on preheated quartz fiber filters. Furthermore, δ^{13}C values of the gas-phase β-pinene and one of its oxidation products, nopinone, were measured using a gas chromatograph coupled to an isotope ratio mass spectrometer (GC-IRMS). β-Pinene was progressively enriched with the heavy carbon isotope due to the kinetic isotope effect (KIE). The KIE of the reaction of β-pinene with ozone was measured to be 1.0026 ($^{O_3}\varepsilon$ 2.6 ± 1.5‰). The δ^{13}C value of total secondary organic aerosol was very similar to that of its precursor (average = -29.6 ± 0.2‰) independent of experiment time. Nopinone, one of the major oxidation products of β-pinene, was found in both the gas and aerosol phases. The gas-phase nopinone was heavier than the initial β-pinene by 1.3‰ but lighter than the corresponding aerosol-phase nopinone. On average, the gas-phase nopinone was lighter by 2.3‰ than the corresponding aerosol-phase nopinone. The second product found in the SOA was detected as acetone, but it desorbed from the filter at a higher temperature than nopinone, which indicates that it is a pyrolysis product. The acetone showed a much lower δ^{13}C (-36.6‰) compared to the initial β-pinene δ^{13}C.

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1. Introduction

[2] Secondary organic aerosols (SOA) formed from the oxidation of volatile organic compounds (VOC) in the atmosphere are important due to their potential impact on human health and global climate [*Fiedler et al.*, 2005; *Jang et al.*, 2006]. The formation of aerosols is a complex multistep process which includes the gas-phase oxidation of aerosol precursors, gas particle partitioning, adsorption of the semi volatile compounds formed [*Seinfeld and Pandis*, 1997] and the oligomerization to higher molecular weight compounds within the particles [*Kalberer et al.*, 2004].

[3] Several laboratory and chamber studies have been performed to study SOA formation. Most of these experiments deal with physical characterization and, to a certain extent, speciation of the different aerosol-phase products [e.g., *Glasius et al.*, 1999; *Jaoui and Kamens*, 2003a; *Lee et al.*, 2006; *Varutbangkul et al.*, 2006]. However, our understanding of the formation process, composition, and properties of these oxidation products is still far from satisfactory.

[4] Analyzing the ratio of stable isotopes can provide additional insight into the extent of chemical and physical processing [*Brenninkmeijer et al.*, 2003; *Goldstein and Shaw*, 2003; *Huang et al.*, 2006; *Rudolph and Czuba*, 2000; *Rudolph et al.*, 2003; *Saito et al.*, 2002]. Oxidation processes in general result in fractionation between the heavy and light isotopes favoring the light isotopes to accumulate in the product whereas the reactant enriches with the heavy isotopes due to the kinetic isotope effect (KIE). As a result, compounds formed from oxidation processes in the atmosphere are isotopically lighter [*Sakugawa and Kaplan*, 1995] whereas their precursors are enriched with heavy isotopes [*Wang and Kawamura*, 2006]. After having determined the KIE in laboratory studies [*Anderson et al.*, 2003, 2004; *Iannone et al.*, 2003; *Cantrell et al.*, 1990; *Rudolph et al.*, 2000; *Iannone et al.*, 2008], it is possible to evaluate the origin of VOCs or their processing in the atmosphere [*Rudolph et al.*, 2003; *Rudolph*, 2007].

[5] At present only few studies exist on stable isotope composition of SOA which, together with gas-phase measurements, can be used to characterize aerosol formation

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and processing. In this study we combine compound specific and whole sample isotope data from both gas-phase and aerosol-phase isotope measurements to trace the isotopic composition from the precursor to the aerosol. We present the kinetic isotope effect associated with the oxidation of the precursor β-pinene with ozone and the compound specific stable carbon isotope composition of SOA formed during the oxidation process. In addition, the temporal variation in the stable carbon isotopic composition of the β-pinene and its oxidation product, nopinone, in both gas and aerosol phase during the oxidation process are presented.

2. Experimental Setup

2.1. The Reaction Chamber

[6] The ozonolysis experiment was conducted at the Jülich large aerosol chamber, which has been described in detail elsewhere [*Mentel et al.*, 1996]. Briefly, the chamber is a 256 m^3 Teflon bag, which is suspended in a dark room. Prior to the experiment, the chamber was flushed with synthetic air (Linde LiPur, quality 6.0, 99.9999% purity). About 600 ppb (~1.0 ml) of the primary component, β-pinene with an isotopic composition of −30.1‰, was injected via the injection port of the chamber using a 100 μl syringe. After allowing the β-pinene to mix for 30 min, ozone was added to the chamber using an electrical discharge ozonizer (operated with pure O_2, quality 5.0, 99.999%), which is connected directly to the chamber. The maximum ozone concentration measured with an ozone monitor (Ansyco O3 41M) was 500 ppb. Temperature and relative humidity (RH) were monitored using a capacitive relative humidity sensor, Vaisala Type HMP235 (Driesen + Kern GmbH, Bad Bramstedt, Germany). Particle size distribution was monitored using a TSI Scanning Mobility Particle Sizer (SMPS; TSI model 3080). Aerosol mass concentrations were calculated from integrated aerosol volume by assuming a spherical shape of particles, and using a density of 1.2 g/cm^3 as determined with an Aerodyne aerosol mass spectrometer (AMS) using procedures described by *DeCarlo et al.* [2004]. The experiment was conducted at 25°C and 2% relative humidity (RH) in the absence of seed aerosol and OH scavenger.

2.2. Sampling

2.2.1. Gas-Phase Sampling

[7] Gas-phase samples were collected at a time interval of 30 min in parallel with the filter samples using precleaned and evacuated silcosteel gas canisters (Restek). About 18 liters of air were sampled within 20 min by pressurizing the canisters to 3 bars. Ozone was removed from the samples by means of a heated silcosteel capillary (120°C) during sampling. Blank measurements were done for the chamber prior to the injection of β-pinene. Gas-phase samples were measured immediately after sampling whenever possible. The longest storage time for the gas samples was 2 days and the effect of storage on the sample isotopic composition of the sample measured after 2 days of storage was 0.4 ± 0.2‰.

2.2.2. Aerosol Sampling

[8] Aerosol samples were taken using quartz fiber filters (Whatman, 47 mm diameter) at a flow rate of 25 l/min for 1 hour. The filters were preheated for 10 hours at 600°C before sampling. Immediately after sample collection, the filters were placed in 55 mm Petri dishes, wrapped in aluminum foil, and stored in a freezer (−18°C) until analysis. Approximately 900 μg carbon was collected on the filter and on average 30 μg carbon was available on the filter cutout for the elemental analysis and for the corresponding stable carbon isotope ratio measurement. Blank samples were taken from the flushed chamber before the injection of β-pinene and 10 min after the injection of the β-pinene (before the injection of ozone). In addition, blank filters were measured and the blank correction was made for total carbon measurements. On average, the concentration and the isotopic composition of carbon of the blank filter were 2 μg and −26.7 ± 1.7‰ respectively. No detectable compound was found during the compound specific stable carbon isotope ratio measurement of the blank filter samples.

2.3. $\delta^{13}C$ Analysis

2.3.1. Gas-Phase Samples

[9] A gas chromatograph coupled to an isotope ratio mass spectrometer via a combustion interface (GC-IRMS) was used for the compound specific stable carbon isotope ratio measurement [*Meieraugenstein*, 1995; *Matthews and Hayes*, 1978; *Rudolph et al.*, 1997; *Simoneit*, 1997]. The instrumentation used in this study, described in detail by *Iannone et al.* [2007], was an Agilent 6890 (1530A) GC coupled to an Isoprime IRMS (GV Instruments, Manchester, UK) via a combustion interface. The GC was equipped with two fused silica columns, an Rtx-1 (Restek Corporation, Bad Homburg, Germany) and BP624 (SGE Scientific, Griesheim, Germany) and a flame ionization detector (FID). The Rtx-1 (105 m × 0.32 mm ID, coated with 100% dimethyl polysiloxane, film thickness 3.0 μm) was used as a primary column for the separation of the components from both gas-phase samples and filter samples. The second column, BP624 (50 m × 0.32 mm ID, coated with Cyanopropylphenyl Polysiloxane, film thickness 1.8 μm) was used for further separation in the presence of compounds coeluting with the peaks of interest. For all the measurements the temperature of the GC oven was programmed from 30°C (5 min hold) to 200°C at 4°C/min (15 min hold).

[10] The GC was connected to a custom built cryosampling thermal desorption system (GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany) for the preconcentration of VOCs. The setup is described in detail by *Iannone et al.* [2007]. In brief, the sampling was achieved cryogenically by passing the gas-phase samples through a silcosteel tube (300 mm × 11 mm ID) packed with glass beads (60–80 mesh) cooled to −150°C. The VOCs were desorbed thermally at a temperature of 240°C and transferred to a second cryotrap (cooled to −170°C) using helium as a carrier gas. The final focusing of the samples was made cryogenically (−80°C) on the first few centimeters of the GC column. This part of the GC was then heated to 250°C at a rate of 12°C/s for subsequent separation of the VOCs on the GC column. After separation, the VOCs were transferred to the combustion interface (quartz tube with a length of 600 mm and 0.5 ID, set temperature = 850°C) packed with copper (II) oxide (CuO) to thermally oxidize the

Table 1. δ^{13}C of Standards Measured From Bulk Samples (Using EA-IRMS) and in Gas-Phase Standard (Using GC-IRMS)[a]

Compound		Our Measurement Using GC-IRMS (±SD)		
Name	Chemical Formula	Total Amount Sampled (ng)	δ^{13}C (±SD)	Agroisolab Measurements (±SD) Using EA-IRMS
Acetone	C_3H_6O	230	−29.8 (0.2)	−29.9 (0.1)
Benzene	C_6H_6	250	−26.9 (0.2)	−27.2 (0.1)
β-Pinene	$C_{10}H_{16}$	170	−29.5 (0.2)	−30.1 (0.1)
Isoprene	C_5H_8	115	−25.2 (0.3)	−25.1 (0.1)
Limonene	$C_{10}H_{16}$	180	−26.8 (0.3)	−27.3 (0.4)
Methacrolein	C_4H_6O	170	−27.7 (0.6)	−28.7 (0.1)
n-Pentane	C_5H_{12}	80	−29.8 (0.2)	−30.8 (0.3)
Nopinone	$C_9H_{14}O$	130	−28.1 (0.1)	−28.1 (0.1)
Toluene	C_7H_8	170	−25.7 (0.3)	−26.8 (0.2)

[a] All values are against VPDB.

respective VOCs quantitatively to CO_2 and water. The water from the combustion of the VOCs was removed in a water trap at −100°C before injection into the MS, whereas the CO_2 was transferred to the mass spectrometer operating in a continuous flow mode for subsequent stable carbon isotope ratio measurement.

[11] The isotopic composition of the samples are reported in the familiar "δ" notation as per mil (‰) which is expressed as

$$\delta^{13}C = \left(\left(R_{sam}\big/R_{std}\right) - 1\right) * 1000 \qquad (1)$$

where R_{sam} is $^{13}C/^{12}C$ of the sample and R_{std} is $^{13}C/^{12}C$ of a standard.

[12] The standard (R_{std}) is a CO_2 reference gas which is calibrated against the international standard Vienna Pee Dee Belemnite (V-PDB). The final δ^{13}C value is therefore reported relative to V-PDB.

2.3.2. Aerosol Samples

[13] For compound specific stable carbon isotope ratio measurements of the aerosol samples, a quartz tube, which has the same length and diameter as the cryotrap 1, was used. A circular filter piece (3 mm in diameter) was cut out from the whole filter and placed in the quartz tube embedded in a plug of silanized glass wool. The quartz tube with the filter inside was placed in the sampling system (by replacing cryotrap 1) and heated to 240°C at a rate of 60°C/min. Similar to the gas-phase sample, the desorbed VOCs from the filter were focused using the second and third cryogenic traps and injected to the GC for separation.

[14] In addition, a stepwise desorption of a single filter was made to characterize the desorption behavior of the desorbed components. For that, a single filter cutout was exposed to different temperatures in a stepwise manner. Eight temperatures between 30°C and 240°C were measured with each temperature step equal to 30°C. The concentration and the δ^{13}C of the desorbed compounds at each temperature step were measured. During each temperature step, the filter was flushed with helium at a flow rate of 7 ml/min for 40min. Between two temperature steps (during the GC run), the quartz tube was cooled down to −10°C to prevent desorption of the remaining component from the filter.

[15] Measurements of the total carbon content and bulk stable carbon isotope composition of the total carbon on the filter samples were performed using an elemental analyzer (Euro Vector, Germany) coupled to a GV-Optima IRMS. For total carbon measurement, circular filter pieces (7 mm diameter) were cut out from the whole filter and loaded into tin capsules that are tightly crimped to avoid any trapping of air that would perturb the combustion. Each capsule is dropped individually into an elemental analyzer and combusted at a temperature of 1080°C. The δ^{13}C of the resulting CO_2 was measured using IRMS. The working standards used were cellulose and graphite with a δ^{13}C value of −22.95‰ and −26.35‰, respectively.

2.3.3. System Calibration

[16] Test measurements were performed using the GC-IRMS both before and after the analysis of the samples. The tests involved analysis of gas standard mixtures containing acetone, toluene, β-pinene, isoprene, limonene, nopinone, *n*-pentane and methacrolein. The gas standards were prepared from bulk compounds in a gas cylinder following the procedure described by *Apel et al.* [1998]. The isotopic compositions of the gas standard compounds were measured by Agroisolab (Agroisolab GmbH, Juelich, Germany) using an elemental analyzer coupled to IRMS (EA-IRMS). The δ^{13}C values of individual compounds measured using a bulk analysis of the liquid samples by Agroisolab and by the GC-IRMS used for this experiment are given in Table 1. For some of the compounds, up to 1‰ difference was observed between our and Agroisolab measurements. The reason for this difference is not clear but could be due to impurities in the liquid compounds used for bulk analysis. In addition, loss processes during the preparation of our standard might have resulted in small fractionation, which may have lead to the observed difference. A certified CO_2 standard with a δ^{13}C of −4.9 ± 0.15‰ was used as a reference gas to calculate the δ^{13}C of the compounds.

3. Results

3.1. Carbon Isotope Composition of Gas-Phase *β*-Pinene and Nopinone

[17] β-Pinene and nopinone were identified in the gas phase and their respective δ^{13}C value was monitored for 8 hours after the injection of ozone (Figure 1). β-Pinene showed an increase in its δ^{13}C value over time (from −29.5‰ to −13.3‰) after the injection of ozone due to the kinetic isotope effect (KIE) associated with the reaction of the β-pinene with ozone.

[18] The KIE of a given chemical reaction is expressed as the ratio of the reaction rate of the light isotope to the

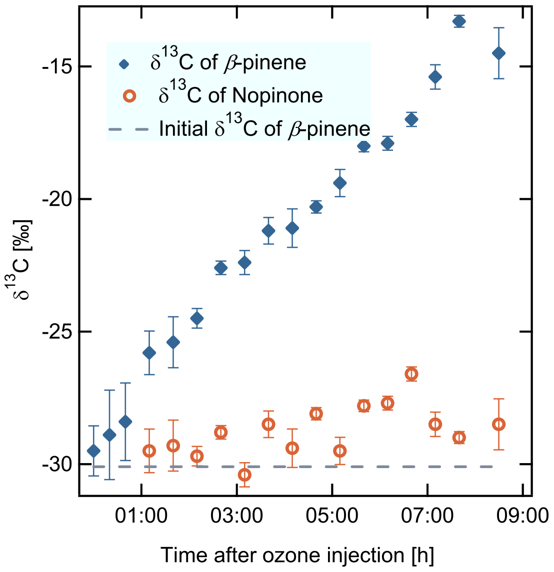

Figure 1. δ^{13}C of β-pinene and gas-phase nopinone after the injection of ozone.

reaction rate of the heavy isotope (KIE = k_{12}/k_{13}). The value of KIE associated with the reaction of β-pinene with ozone can be calculated from the measured δ^{13}C value of β-pinene and its concentration using the following expression [*Anderson et al.*, 2003; *Rudolph*, 2007].

$$\ln\left[{}^{12}C_t\Big/{}^{12}C_0\right] = \left(\frac{k_{12}/k_{13}}{\left(1-k_{12}\big/k_{13}\right)}\right)\times\ln\left[\frac{\delta^{13}C_t+1000}{\delta^{13}C_0+1000}\right] \tag{2}$$

where k_{12} and k_{13} are the reaction rates of molecules containing only ^{12}C and ^{13}C, respectively, $^{12}C_0$ and $^{12}C_t$ are the concentrations of ^{12}C of β-pinene at time t = 0 and t; and $\delta^{13}C_0$ and $\delta^{13}C_t$ are the isotopic composition of β-pinene at time t = 0 and t, respectively.

[19] Plotting $\ln({}^{12}C_t/{}^{12}C_0)$ versus $\ln((\delta^{13}C_t + 1000)/(\delta^{13}C_0 + 1000))$ gives a straight line with a slope of KIE/(1 − KIE). The KIE can then be calculated from the slope of the linear least squares fit as

$$KIE = \left(\frac{slope}{(1+slope)}\right) \tag{3}$$

[20] The resulting KIE of the above expression is in general a very small number. Therefore it is usually expressed as

$$^{O_3}\varepsilon = (KIE - 1)\times 1000\ ‰ \tag{4}$$

[21] Figure 2 shows the plot according to equation (2) for the KIE calculation. A KIE value of 1.0026 ± 0.0015 was calculated from the slope of the regression line in Figure 2 and the corresponding $^{O3}\varepsilon$ value is 2.6 ± 1.5‰.

[22] To our knowledge, no measured KIE value for the reaction of β-pinene with ozone has been reported yet. In an effort to compare our measured $^{O3}\varepsilon$ data with literature, a theoretical $^{O3}\varepsilon$ for the reaction of β-pinene with ozone was estimated from the inverse dependence on carbon number (N_C) described by *Rudolph* [2007] as

$$^{O_3}\varepsilon(‰) = (34.0 \pm 1.0)‰/N_C \tag{5}$$

[23] From this relationship, the estimated $^{O3}\varepsilon$ for the reaction of β-pinene (C10 compound) with ozone was higher (3.4 ± 0.1‰) but within the range of uncertainty of the measured value.

[24] The δ^{13}C value of gas-phase nopinone ranged between −30.4‰ and −26.6‰ (Figure 1). In general, nopinone in the gas phase was depleted in the heavy isotope compared to the β-pinene remaining in the chamber.

3.2. Concentration and δ^{13}C of Total Carbon in the SOA

[25] The total organic carbon concentration in the SOA and the respective SOA mass concentrations derived from SMPS data are presented in Figure 3. The total organic carbon concentration in the SOA changed from 2 μg/m^3 to 540 μg/m^3 at the maximum aerosol mass, while the total SOA mass derived from the SMPS data ranged from 5 μg/m^3 to 600 μg/m^3. Although the SOA mass concentration derived from the SMPS is expected to be higher than the total carbon concentration due to the presence of oxygen in the SOA, the observed difference is only 11%. This small difference could be due to loss of particles on the SMPS during sampling and also the presence of particles with diameters larger than the cut point of the SMPS that can easily be sampled with the filter sampling. The maximum SOA yield for this experiment was calculated to be 28 (±6)%. This value is in good agreement with previous

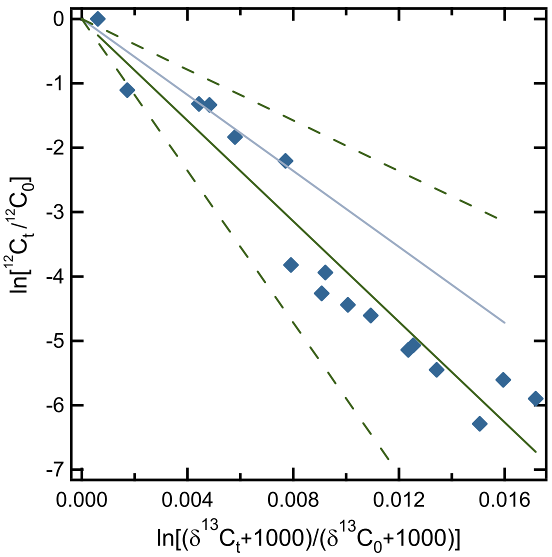

Figure 2. Plot used for the determination of KIE from the experimental data. Diamonds are experimental data, the dark solid line is the fit to the experimental data, and dashed lines indicate the standard deviation given by the fit. The gray solid line is the slope that gives the KIE value calculated from the inverse relationship of KIE on the carbon number given by *Rudolph* [2007]. The slope for this graph is −390.6 ± 223 with R^2 = 0.927.

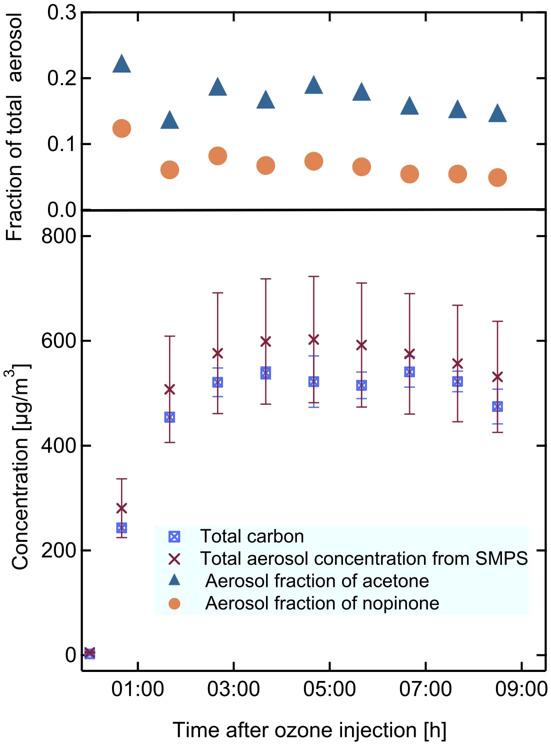

Figure 3. Temporal variation of the concentration of total carbon from the filter measurement and total aerosol mass concentration derived from the SMPS data (bottom) and fraction of aerosol carbon attributed to the aerosol-phase nopinone and acetone (top).

studies reporting aerosol yields of 26% [*Jaoui and Kamens*, 2003b] and 32% [*Hoffmann et al.*, 1997].

[26] The $\delta^{13}C$ value of the total carbon ranged between −30.1‰ and −29.3‰ with an average value of −29.6‰. This value is very close to the initial β-pinene injected into the chamber which was −30.1‰

3.3. Composition and Compound Specific $\delta^{13}C$ Value of SOA

3.3.1. Identification of Compounds in SOA

[27] From the compound specific GC-IRMS measurement, several peaks were detected, however, only two major peaks, which were identified as nopinone and acetone, had enough signal intensity to be used for data analysis. While nopinone has previously been measured in the aerosol as a reaction product of β-pinene with ozone [*Winterhalter et al.*, 1999; *Jaoui and Kamens*, 2003b; *Lee et al.*, 2006], the acetone signal from aerosol samples is unexpected due to the high vapor pressure of acetone. Therefore additional peak identification and characterization was necessary for the filter samples.

[28] In order to verify the identification of the peak as acetone, filters were analyzed using GC-MS. The retention time matched very well with that of acetone and the mass spectrum also confirmed the identification of this peak as acetone. Blank measurements of the desorption unit were performed to exclude contaminations of the GC-IRMS system as a possible source for the observed acetone signal. Blank filters were also analyzed to check the presence of acetone on the filters themselves and no acetone was detected. In order to rule out the possibility that the acetone signal might be a result of a reaction of ozone with the wall or any contamination in the chamber, an additional experiment was performed. For this additional experiment the chamber was flushed with clean air as described above and 500 ppb of ozone was added to the flushed chamber. The maximum aerosol mass produced in this experiment was 0.25 $\mu g/m^3$, which is only 0.05% of the maximum aerosol mass concentration formed during the β-pinene experiment. For this blank experiment, the acetone concentration from filter samples was below the detection limit of 10ng.

[29] Having ensured that the acetone is a signal directly related to the SOA from β-pinene, the stepwise thermal desorption result was used to further characterize the origin of the acetone peak. As shown in Figure 4, only 60% of the acetone was desorbed at a temperature of 120°C whereas more than 90% of nopinone desorbed at the same temperature, showing that the acetone needed a higher temperature to be desorbed from the filter than nopinone. Moreover, while the change in $\delta^{13}C$ value of the acetone was small

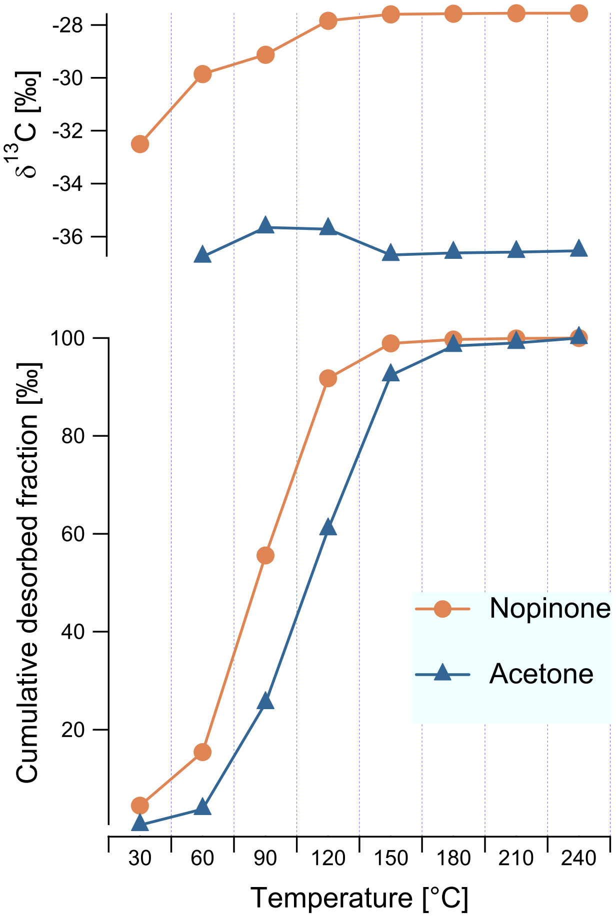

Figure 4. Cumulative desorbed fraction of acetone and nopinone from one filter sample exposed to different temperatures in a stepwise manner (bottom graph). The upper graph shows corresponding $\delta^{13}C$ of the desorbed fraction.

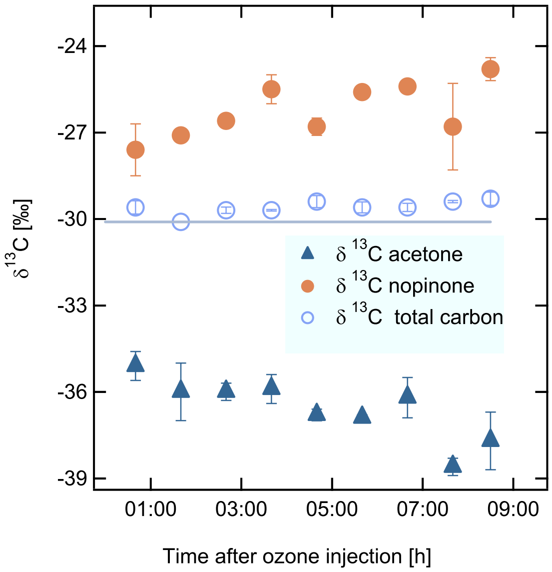

Figure 5. δ^{13}C measurement of nopinone and acetone in the aerosol phase and total carbon. The gray line indicates the initial δ^{13}C of β-pinene injected.

(0.5‰), the δ^{13}C of nopinone showed a progressive isotopic enrichment by 4‰ (Figure 4).

[30] The maximum gas-phase concentration of nopinone during the thermal desorption was 13 mg/m^3 at a temperature of 90°C and the saturation concentration of nopinone is 5 g/m^3 at 25°C. This suggests that desorption of nopinone from the filter was not influenced by the saturation concentration inside the desorption tube.

[31] As shown in Figure 4, at 180°C, both acetone and nopinone desorbed completely resulting in leveled cumulative concentration and δ^{13}C values which shows that at a temperature of 240°C, the temperature used for all filters analyzed, all the components are completely removed from the filter which is critical for isotope measurement.

3.3.2. Composition of SOA

[32] On average, nopinone contributed 7% of the total carbon on the filter (Figure 3), which is in agreement with literature data [*Jaoui and Kamens*, 2003b]. Acetone accounts for 17% of the total carbon, showing the importance of the contribution of this compound or compound class to the total aerosol mass. The fact that only 23% of the total aerosol mass is covered with the compounds specific measurement leaves some gap in the understanding of SOA formation and processing. One of the reasons for this low percentage is the limitation of the GC with regard to measuring polar compounds and other high molecular weight compounds. Other complementary techniques such as liquid chromatography coupled to isotope ratio mass spectrometer (LC-IRMS) could be used in such cases.

3.3.3. δ^{13}C Value of Compounds in SOA

[33] The change in the δ^{13}C value of acetone and nopinone in the aerosol is given in Figure 5. The δ^{13}C value of acetone decreased by 4‰ over 8 hours (from −35.1‰ to −38.6‰) after the reaction of β-pinene with ozone was started. The δ^{13}C value of aerosol-phase nopinone increased by 2.8‰ (from −27.6‰ to −24.8‰). The acetone was generally depleted in the heavy carbon isotope compared to both the initial β-pinene injected (−30.1‰) and nopinone.

[34] The δ^{13}C value of nopinone in the aerosol phase was higher than the δ^{13}C value of gas-phase nopinone. On average the difference between the gas and aerosol-phase nopinone δ^{13}C value was 2.3 ± 0.8‰.

4. Discussion

[35] In a closed system, with only one product formed which is not transferred further, the δ^{13}C value of the product at the end of the reaction should be equal to the initial δ^{13}C value of the reactant [*Schmidt et al.*, 2004]. However, the measured gas-phase δ^{13}C value of nopinone was −28.5 ± 0.8‰ at the end of the experiment which is higher than the initial β-pinene δ^{13}C by 1.6‰. One possible explanation for the observed enrichment of nopinone is the loss of one carbon atom from β-pinene during the ozonolysis reaction to form nopinone. The initial reaction of the β-pinene ozonolysis proceeds via O_3 addition to the double bond ($C = C$) to form an energy-rich ozonide which decomposes mainly to a C9 compound (nopinone) and a C1 Criegee intermediate. Due to the KIE a β-pinene molecule with a double bond connecting only ^{12}C atoms reacts faster. Subsequently light carbon is removed first. The remaining 9 carbons (nopinone) will thus be heavier compared to the initial β-pinene if the initial distribution of carbon isotopes within β-pinene is equal.

[36] Another possible explanation for the observed enrichment of nopinone is loss of nopinone during the reaction. There are two possible loss processes for gas-phase nopinone in the system. The first is the partitioning of the nopinone into the particle phase. On average, the observed δ^{13}C of gas-phase nopinone was lower than the aerosol-phase nopinone by 2.3‰. This shows that the gas particle partitioning decreased the δ^{13}C value of nopinone in the gas phase. Therefore gas particle partitioning cannot explain the observed enrichment of gas-phase nopinone.

[37] The second loss process is oxidation of nopinone in the gas phase with ozone and OH radicals. The reaction of nopinone with ozone is a very slow process ($k = 5 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} [*Calogirou et al.*, 1999]). Therefore this reaction is not expected to significantly affect the concentration and isotopic composition of nopinone. The other oxidant present in the chamber is OH, which is formed from the reaction of β-pinene with ozone [*Hoffmann et al.*, 1997]. The reaction rate of nopinone with OH is much faster ($k = 1.7 \pm 0.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) compared to ozone. The minimum lifetime of nopinone calculated using the Master Chemical Mechanism (MCM [*Jenkin et al.*, 2003; *Saunders et al.*, 2003]) for this experiment due to the OH radical was about 20 hours. Therefore the reaction of nopinone with OH may affect the concentration and subsequently the δ^{13}C value of nopinone in the gas phase.

[38] The δ^{13}C value of the total carbon was on average −29.6 ± 0.3‰ which is not significantly different from the initial δ^{13}C value of β-pinene injected. Unfortunately there is no other literature data on isotopic composition of biogenic SOA to compare with our result.

[39] The δ^{13}C values of the individual compounds found in the SOA showed a clear dependence on reaction time and differ from the total aerosol carbon δ^{13}C. The δ^{13}C value of

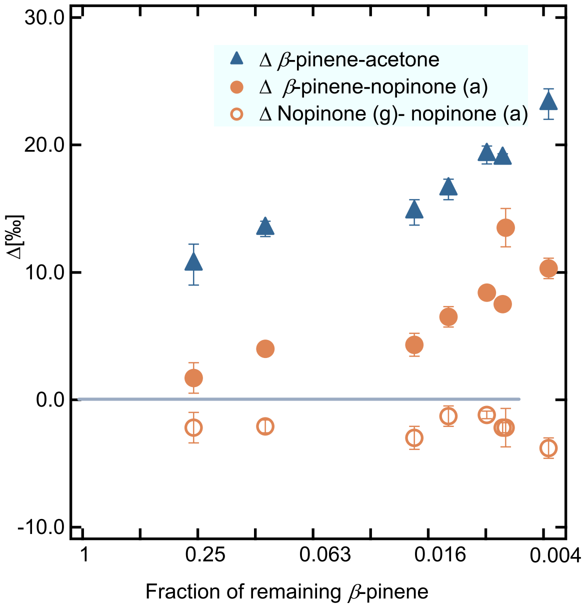

Figure 6. Enrichment factor (Δ) for β-pinene and aerosol-phase acetone and nopinone (nopinone (a)) as a function of β-pinene remaining in the gas phase. Also given is the enrichment factor for gas-phase nopinone (nopinone (g)) and aerosol-phase nopinone. Δ is calculated as $\delta^{13}C_{reactant} - \delta^{13}C_{product}$ at time *t*.

acetone was much smaller (−35.1‰ to −38.6‰) than that of the total carbon whereas the $\delta^{13}C$ value of nopinone in the aerosol phase was higher (−27.6‰ to −24.8‰). The difference in isotopic composition of the individual compounds could be indicative of different formation process of these compounds. From the stepwise thermal desorption, it is also evident that acetone is a thermal decomposition product from aerosol-phase compounds.

[40] Although a clear explanation is still needed, two hypotheses are proposed to explain the source of acetone in the aerosol phase. Firstly, acetone could be a thermal decomposition product of an oligomer. Recently high molecular weight compounds were identified in SOA and oligomerization of low molecular weight compounds was proposed as one of the possible formation pathways for high molecular weight compounds [*Kalberer et al.*, 2004; *Tolocka et al.*, 2004]. Low molecular weight compounds are expected to be depleted in their $\delta^{13}C$ value as they are secondary or tertiary products of β-pinene oxidation. Therefore thermal decomposition of such oligomers could result in isotopically light acetone. The second hypothesis is that acetone is formed from a partial decomposition of high molecular compounds which contain a C = O functional group. During the reaction of β-pinene with ozone, the initial reaction proceeds via ozone addition to the exocyclic C = C double bond. Due to the KIE C = C bonds which connect light carbons will be attacked first by ozone resulting in a ^{13}C depleted C = O site. If this C = O site of a larger molecule breaks off to form acetone during the thermal decomposition, the produced acetone is expected to be lighter compared to the other part of the molecule. Both hypotheses are consistent with the results from the stepwise thermal desorption since both will result in low apparent volatility of acetone and little dependence of the released acetone $\delta^{13}C$ on temperature. Further investigations are needed to identify the origin of acetone in the SOA.

[41] The enrichment factor, $\Delta_{r/p}$ between the precursor β-pinene and the measured oxidation products in the aerosol phase were determined to further estimate the extent of fractionation of the different processes, which for atmospheric samples, could be used for studying chemical aging of air masses.

[42] The difference between the $\delta^{13}C$ value of β-pinene and the $\delta^{13}C$ value of its oxidation products can be expressed using an enrichment factor, Δ. In general, Δ is expressed as

$$\Delta_{r/p} = \delta_r - \delta_p^i \qquad (6)$$

where $\Delta_{r/p}$ is the enrichment factor between the reactant (r) and its product (p), δ_r and δ^i_p are the isotopic value of the reactant and of the resulting product i, at time t, respectively.

[43] The Δ values between the precursor β-pinene and its oxidation products in the aerosol phase are graphically summarized in Figure 6. As shown in Figure 6, the enrichment factor for the gas particle partitioning of nopinone is independent of reaction time while the enrichment factors between the β-pinene and its oxidation products increase with decreasing fraction of β-pinene remaining in the gas phase. The highest enrichment factor was observed between acetone from the aerosol sample and gas-phase β-pinene.

5. Conclusions

[44] The $\delta^{13}C$ values of β-pinene and its major oxidation products in the gas and aerosol phase were determined for the reaction of β-pinene with ozone. For this reaction, a KIE value of 1.0026 ± 0.0015 ($^{O3}\varepsilon = 2.6 \pm 1.5$‰) was measured. The measured KIE can be used for photochemical aging studies of β-pinene emitted from plants. However, its main oxidation product, nopinone, did not show a strong fractionation. The gas particle partitioning of nopinone resulted in an enrichment of the aerosol-phase nopinone by 2.3‰ which was not as high as the enrichment factor between β-pinene and gas-phase nopinone.

[45] In general, the $\delta^{13}C$ of total organic carbon on the filter was slightly higher (0.5‰) than the initial β-pinene injected into the chamber and showed no temporal variation. Nevertheless, considerable differences in $\delta^{13}C$ values between different species identified in the SOA have been observed. The $\delta^{13}C$ value of nopinone in the aerosol was higher by up to 3.3‰ relative to the total carbon whereas the acetone was lighter by 7‰ at the end of the experiment.

[46] Due to the limited number of stable isotope studies of SOA, it is currently not possible to identify the origin of the acetone measured from the SOA. However, from the high temperature needed to desorb the compounds from the filter, it is evident that the acetone is a thermal degradation product of a higher molecular weight compound or oligomer.

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