C$_1$—C$_{15}$ Alkyl Nitrates, Benzyl Nitrate, and Bifunctional Nitrates: Measurements in California and South Atlantic Air and Global Comparison Using C$_2$Cl$_4$ and CHBr$_3$ as Marker Molecules[†]

MANFRED SCHNEIDER,[‡,§]
OLIVER LUXENHOFER,[‡]
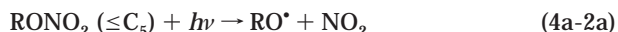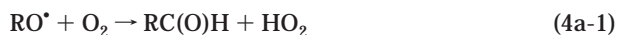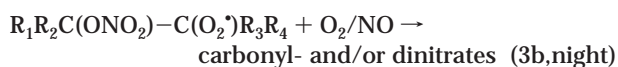ANGELA DEISSLER,[‡,‖] AND
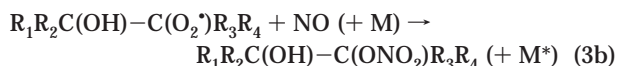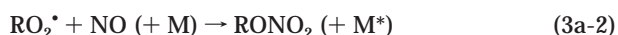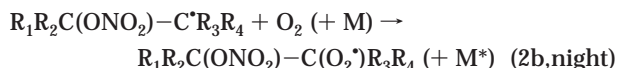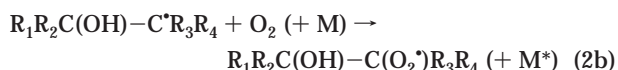KARLHEINZ BALLSCHMITER*,[‡,‖]

Department of Analytical and Environmental Chemistry, University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany, and Center of Technology Assessment in Baden-Wuerttemberg, Industriestrasse 5, D-70565 Stuttgart, Germany

Measurements of C$_1$—C$_{15}$ alkyl nitrates, perchloroethylene, and bromoform at two different sampling sites near *Santa Cruz, CA*, were conducted in 1995. The halocarbons were used as marker molecules to differentiate the air parcels collected into marine and continental groups. The average concentration of $\sum n/i$-C$_3$—C$_{12}$ alkyl nitrates at the California Coast (19.3 pptv) was lower than the levels obtained in the coastal mountains (53.9 pptv). This difference was shown to be most significant for the long chain n/i-C$_6$—C$_{12}$ alkyl nitrates. It is concluded that the $\geq$C$_6$ alkyl nitrates in continental air can contribute 1—2% to the total NO$_y$. The results are summarized together with earlier data sets to give a picture of contemporary levels and of the global occurrence of C$_3$—C$_{12}$ alkyl nitrates. In comparison with South Atlantic air (3.5 pptv), pattern analysis of *n*-alkyl nitrates suggests a marine source of primary *n*-alkyl nitrates. It is also shown that liquid chromatographic preseparation of the air sample extracts leads to a fraction that contains more polar organic nitrates. Several alkyl dinitrates and benzyl nitrate are detected in air samples from California, the South Atlantic region, and Europe. The vicinal alkyl dinitrates show increased abundance in a nighttime sample. The relative abundance of benzyl nitrate compared to alkyl (mono) nitrates is used as a tool for global air mass characterization.

Introduction

We have recently focused our work on the atmospheric fate of biogenic and geogenic hydrocarbons by the global determination of their tropospheric photooxidation products that are abundant in the form of organic nitrates (alkyl nitrates, aromatic nitrates, and bifunctional nitrates; *1*). The atmospheric chemistry of organic nitrates as part of the pool of "odd nitrogen" (NO$_y$) has been reviewed by Roberts (*2, 3*). The basic atmospheric chemistry of alkanes and alkenes leading to alkyl nitrates and bifunctional organic nitrates can be summarized as follows:

$$RH + OH \rightarrow R^{\bullet} + H_2O \tag{1a}$$

$$R_1R_2C{=}CR_3R_4 + OH \rightarrow R_1R_2C(OH){-}C^{\bullet}R_3R_4 \tag{1b}$$

$$R_1R_2C{=}CR_3R_4 + NO_3 \rightarrow$$
$$R_1R_2C(ONO_2){-}C^{\bullet}R_3R_4 \tag{1b,night}$$

$$R^{\bullet} + O_2 \ (+\ M) \rightarrow RO_2^{\bullet} \ (+\ M^*) \tag{2a}$$

$$R_1R_2C(OH){-}C^{\bullet}R_3R_4 + O_2 \ (+\ M) \rightarrow$$
$$R_1R_2C(OH){-}C(O_2^{\bullet})R_3R_4 \ (+\ M^*) \tag{2b}$$

$$R_1R_2C(ONO_2){-}C^{\bullet}R_3R_4 + O_2 \ (+\ M) \rightarrow$$
$$R_1R_2C(ONO_2){-}C(O_2^{\bullet})R_3R_4 \ (+\ M^*) \tag{2b,night}$$

$$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \tag{3a-1}$$

$$RO_2^{\bullet} + NO \ (+\ M) \rightarrow RONO_2 \ (+\ M^*) \tag{3a-2}$$

$$RO_2^{\bullet} + NO_2 \ (+\ M) \rightarrow RO_2NO_2 \ (+\ M^*) \tag{3a-3}$$

$$R_1R_2C(OH){-}C(O_2^{\bullet})R_3R_4 + NO \ (+\ M) \rightarrow$$
$$R_1R_2C(OH){-}C(ONO_2)R_3R_4 \ (+\ M^*) \tag{3b}$$

$$R_1R_2C(ONO_2){-}C(O_2^{\bullet})R_3R_4 + O_2/NO \rightarrow$$
$$\text{carbonyl- and/or dinitrates} \tag{3b,night}$$

$$RO^{\bullet} + O_2 \rightarrow RC(O)H + HO_2 \tag{4a-1}$$

$$RONO_2 \ (\leq C_5) + h\nu \rightarrow RO^{\bullet} + NO_2 \tag{4a-2a}$$

$$RONO_2 \ (> C_5) + OH \rightarrow$$
$$\text{bifunctional nitrates, polar products} \tag{4a-2b}$$

These reaction schemes focus on the possible atmospheric formation processes of organic nitrates. However, it is important to keep in mind that the main reaction pathway of alkylperoxy radicals (RO$_2$) leads to the formation of carbonyl compounds and HO$_2$ (4a-1). Besides that, RO$_2$ undergo a concurring reaction to form alkyl nitrates from alkanes (3a-2) and vicinal bifunctional organic nitrates from alkenes (3b). The yield α of alkyl nitrate formation from RO$_2$ ($\alpha = k_{3a-2}/k_{3a-1} + k_{3a-2}$) depends on the alkyl chain length, temperature, and pressure. These yields increase continually with the alkyl chain length and are reported to reach a maximum of 35% at C$_9$ (*4*). The processes of removal of alkyl nitrates from the atmosphere and the resulting lifetimes also depend on the length of the alkyl chain. Photodissociation (4a-2a) is known to be the major decomposition process for $\leq$C$_5$ alkyl nitrates. Reaction with OH radicals (4a-2b) adds to the photolysis and becomes dominant for larger alkyl chains. Short-chain alkyl nitrates have atmospheric lifetimes

ranging from weeks to several days (C_2–C_5, respectively) and have decreasing lifetimes with further increasing alkyl chains (5, 6).

Bifunctional organic nitrates result from daytime and nighttime reactions of unsaturated hydrocarbons initiated by OH and NO_3 addition, respectively (reaction 1b) (7, 8). Vicinal hydroxy-, carbonyl- and dinitrates (reaction 3b) are possible products. The abundance of 15 C_2–C_6 alkyl dinitrates, including isomeric cyclohexyl dinitrates, has been reported in urban air (9). Henry's law constants and resulting lifetimes for several C_2–C_4 hydroxynitrates have been published. Wet deposition and reaction with OH radicals are the most significant loss processes of these species (8). The physicochemical constants describing the environmental behavior (K_{OW}, Henry's law) have been determined for 26 dinitrates (10). O'Brien et al. reported the first measurement of bifunctional organic nitrates (11). Organic peroxynitrates, formed via reaction 3a-3, show in general high thermal instability. However, it has been shown recently that particular organic moieties may lead to an increase in stability (12).

Atlas first reported levels of C_4–C_5 alkyl nitrates in marine air (13). Since then, the atmospheric occurrence of alkyl nitrates has been discussed by several authors (11, 14–25). We have analyzed the atmospheric occurrence of branched (i-) and n-alkyl nitrates up to carbon numbers C_{17} in clean and polluted air (20, 21, 26, 27).

The purpose of this work is to report gas-phase C_1–C_{15} n- and isoalkyl nitrates in California air with the first inter-hemispheric comparison of alkyl nitrates including longer alkyl chains. In addition, we present the first results on the gas chromatographic separation and mass selective (GC–MS) detection of bifunctional organic nitrates and benzyl nitrate in air samples from California, the South Atlantic, and central Europe.

Experimental Section

Sample Locations and Weather Conditions. The air samples in California were collected in collaboration with the Institute of Marine Sciences from the University of California at Santa Cruz (UCSC) in August 1995. The main site for air sampling (36°57′ N/122°03′ W; 10 samples) was located on top of a cliff directly at the coast 5 m above sea level and 50 m from UCSC Long Marine Lab Meteorological Station. Relevant weather data from this station, i.e., temperature, pressure, wind speed, and direction, were accessible in 10-min intervals. Four additional air samples have been taken on the RV *Shana Rae* out in the Pacific Ocean (2–5 mi away from the coordinates given above). The weather conditions at the sampling days (August 20, 22, 24, 25, and 29, 1995) were stable, e.g., the 24-h air temperature variation at the coast for each sampling day was 15 ± 3 °C. All analyzed samples were taken during daytime from 9 a.m. to 5 p.m. with strong westerly winds of 4–9 m/s. In addition, four air samples (August 29, 1998) were taken near Boulder Creek, CA, in the rural Big Basin Redwoods State Park (37°07′ N/122°07′ W) south of the San Francisco Bay Area and approximately 25 mi away from the coastal Santa Cruz sampling site. The temperature was on average 10 °C higher than at the coast with slow northwesterly winds of 0.6 m/s.

The weather conditions for the rural-continental air samples (six daytime and one nighttime sample; 48° N/10° E) taken near the city of Ulm, Germany, in June 1995 were obtained from a nearby weather station of the German Weather Service (Deutscher Wetter Dienst Ulm) and have been described in detail (1). In short, the daytime samples were collected between 9 a.m. and 6 p.m. with average winds of 1–2 m/s. The overall wind direction for the characterization of these samples was northwest, taking into account the 10-h average wind direction before sampling because of the frequently changing winds, characteristic of a continental pattern. The sampling volumes were 70–75 m^3 at temperatures of approximately 20 °C. The nighttime sample was taken from 0 to 3 a.m. at a temperature of 13 °C.

Air samples in the South Atlantic were taken in May/June 1994 on board the RV *Meteor* from Namibia to Argentina (latitudinal range 15° S–40° S). Thirteen sampling locations across the Atlantic Ocean covering the two major circulation zones, i.e., the southeast trade wind region and the westwind belt, provided a spatial concentration profile. The exact locations including air temperatures, wind speed, and directions have been described recently (27).

Air Sampling and Analysis of Alkyl Nitrates and Halocarbons. Eighteen air samples from five different sampling days have been analyzed. Low-volume (8–30 L) and high-volume (100–200 m^3) sampling was applied to collect short-chain alkyl nitrates and long-chain alkyl nitrates (and dinitrates), respectively. We recently described both sampling procedures including sample workup and quantitation (27). Hence, we report here only important steps and modifications. Low-volume air samples for the thermal desorption–gas chromatographic analysis (TD–GC) of C_1–C_5 alkyl nitrates, C_2Cl_4, and $CHBr_3$ with electron capture detection (ECD) were collected using Tenax as the adsorbens. Two Tenax traps (connected in series) were used to control sampling efficiency. A HP–VOC capillary column (60 m; i.d. 0.32 mm; d_f 1.8 μm; Hewlett-Packard, Palo Alto, CA) was used with hydrogen as the carrier gas (50 kPa) and a temperature program of 45 °C (2 min), rate 3 °C/min to 250 °C.

The ≥C_6 alkyl nitrates were collected by high-volume sampling on silica gel (two 100-g layers) with a preconnected glass fiber filter. A self-made carbon-covered silica gel sampling material (CCSG–ANGI–SORB 10B) was simultaneously used to compare sampling efficiencies to pure silica gel. This material retains water to a much lesser extent than silica gel. It is producible in kilogram amounts in our laboratory and is nearly as easy to clean for air sampling as silica gel (28, 29). Liquid desorption of alkyl nitrates with pentane:dichloromethane 4:1 (v/v) from CCSG is achieved by the same procedure as described for silica gel with equal recoveries (27, 28). Liquid chromatography (LC) of the reduced sample extract with pentane on silica gel presparates the alkyl nitrates from interferences in the subsequent GC separation (27). After 19 mL of pentane (fraction 1a), the alkyl nitrates elute in the following 35 mL of pentane (fraction 1b). More polar compounds of the air samples (e.g., alkyl dinitrates and benzyl nitrate) are eluted in fraction 2 with 35 mL of pentane/acetone (10:1). The fractions were reduced to ≈500 μL before GC separation. GC analysis of the alkyl nitrate fraction 1b was performed as described (27). Helium was used as the carrier gas (150 kPa) in the case of MS detection. All other important analytical steps, e.g., quantitation of the sum of ≥C_6 n- and i-alkyl nitrates ($\Sigma n/iC_6$–C_{12}) with internal standard as well as the GC retention characteristics of more than 80 alkyl nitrates have been reported (27, 30).

Synthesis of Aromatic Nitrates and Alkyl Dinitrates. Reference solutions of benzyl nitrate (BzN) and o-, m-, and p-methylbenzyl nitrates were prepared by a modified nucleophilic substitution reaction. The corresponding (methyl)benzyl bromide is eluted with hexane/acetone (10:1) on silica gel covered with silver nitrate (1). The procedure results in the complete conversion of all aromatic bromides to the corresponding aromatic nitrates.

Hexane solutions of alkyl dinitrates can be derived via microsynthetic esterification of the precursing alkyl diols with a mixture of HNO_3 and H_2SO_4 as reported for the synthesis of alkyl mononitrates (30). We synthesized the vicinal 1,-2C_2-, 1,2C_3-, and 2,3C_4-dinitrates (e.g., 2,3C_4 = 2,3-dinitroox-
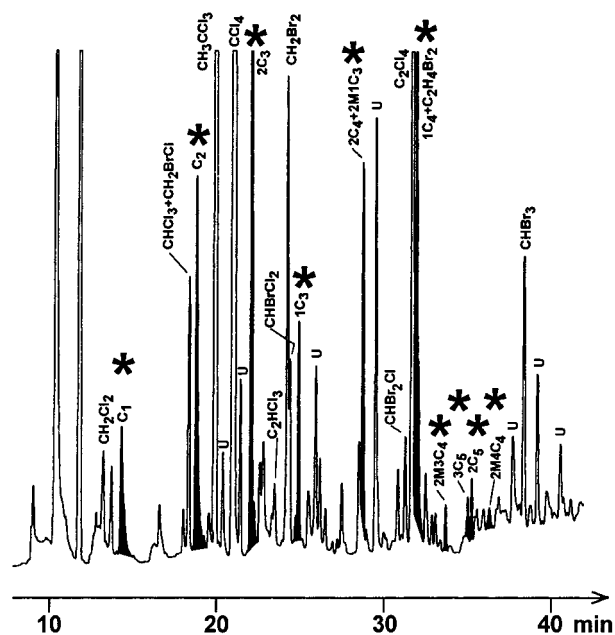
FIGURE 1. Tenax thermal desorption—HRGC(HP—VOC)/ECD: C_1—C_5 alkyl nitrates and halocarbons detected in 30.5 L of marine air at the California Coast. U, unknown.

ybutane). $1,3C_4$-Dinitrate and several α,ω-dinitrates (O_2NO—$(CH_2)_n$—ONO_2, $n = 3$–8) were also synthesized. All solutions of aromatic nitrates or alkyl dinitrates were characterized mass spectrometrically after GC separation. The electron impact (EI) mass spectra were obtained at an ion source temperature of 190 °C. The GC/MSD parameters were the same as described below.

Analysis of Aromatic Nitrates and Alkyl Dinitrates in High-Volume Air Samples. Recovery studies showed that the above-described LC preseparation elutes the aromatic nitrates and the alkyl dinitrates into fraction 2. Air samples from six different sampling locations have been analyzed. Besides the California samples and marine air samples from the South Atlantic region, rural-continental air samples from central Europe (Ulm, Germany) are included (see sampling locations). The same amount of internal standard as to fraction 1b (10 ng of heptachloropropane) was added to fraction 2 prior to analysis on a HP5890 GC (Hewlett-Packard, Palo Alto, CA) with ECD or MSD (HP5970). EI—MS (70 eV) was used in the SIM mode (see Results for specific masses). The compounds in fraction 2 are more polar than alkyl mononitrates. A CP—Sil 2 capillary column (55 m; i.d. 0.25 mm; d_f 0.25 μm; temperature program 40 °C (3 min), rate 3 °C/min to 250 °C; Chrompack, Middelburg, The Netherlands) was used for separation as this new stationary phase of squalan-type is highly selective for hydrophobic interactions. Thus, it reduces the chromatographic stress of polar and thermolabile compounds, e.g., hydroxy nitrates. In addition, m-, p-, and o-methylbenzyl nitrates are fully separated on CP—Sil 2 while the meta and para isomers coelute on a methyl-polysiloxane stationary phase.

Results and Discussion

Detection of C_1—C_{15} Alkyl Nitrates and Assessment of the Analytical Methods. The analysis of the low-volume air samples did not cause any problems regarding sampling capacity for $\geq C_3$ alkyl nitrates at the predominant air temperatures. Figure 1 shows the chromatogram of the air sample with the highest sampling volume. Alkyl nitrate peaks are painted black and labeled with an asterisk (for the structure-specific peak labeling, see special nomenclature section). The detected halocarbons are assigned with their

chemical formula. $2C_3$-Nitrate and perchloroethylene (C_2Cl_4) showed a breakthrough (relative amount in the second sampling trap compared to the first) of <50%. Both traps were always quantified to ensure no losses. Molecules eluting earlier than $2C_3$-nitrate (including C_1- and C_2-nitrate) could not be quantified.

It has been reported that n-butyl nitrates are approximately four times more abundant than n-pentyl nitrates and that an additional pentyl nitrate isomer was detectable (presumably 2-isopentyl nitrate) (13). Our results obtained here confirm these findings. In Figure 1, the excess of butyl nitrates over pentyl nitrates is apparent, and two out of four possible isopentyl nitrates are detected. 2-Isopentyl nitrate ($2M3C_4$-nitrate) is always the most abundant isopentyl nitrate, sometimes exceeding the $2C_5$-nitrate peak. The isomerism of all possible precursing C_1–C_5 alkanes leads to 16 possible C_1–C_5 n- and i-alkyl nitrates (30), of which 11 could be assigned in Figure 1. Two of the "missing" five compounds are tertiary alkyl nitrates ($2M2C_3$ = $tert$-butyl nitrate and $2M2C_4$) that cannot be detected with this method because of their instability. The remaining three ($1C_5$, $2M1C_4$, and $2,2M1C_3$) are too low in concentrations with $1C_5$ occasionally detectable. $2C_4$- and $2M1C_3$-nitrate coelute with an expected small contribution of $2M1C_3$ to the sum of both (13). To our knowledge, this pair of isomers could not be separated by gas chromatography so far. The CP—Sil2 column (see Experimental Section) is able to separate $2C_4$- and $2M1C_3$-nitrate with $2C_4$ eluting first. The ratio of $2C_4/2M1C_3$ in air is approximately 10/1 (data not shown).

The decreasing concentrations of alkyl nitrates with increasing alkyl chains require high-volume sampling for $\geq C_6$ alkyl nitrates. Figure 2 depicts the gas-phase fraction of alkyl nitrates detected after high-resolution GC of the LC preseparation fraction 1b. The 200 m³ air sample shown was collected simultaneously with the low volume Tenax sample depicted in Figure 1. The numerous alkyl nitrate peaks illustrate why a simple systematic nomenclature is useful to handle peak labeling. All n-alkyl nitrates from C_6–C_{15} are assigned. Almost all the remaining peaks are iso-alkyl nitrates (27), and we were able to structurally assign several iso-hexyl and -heptyl nitrates in Figure 2. The air aliquot analyzed is approximately 1900 L, 60 times the volume analyzed in Figure 1. This explains our general finding that long chain alkyl nitrates $\geq C_6$ are very difficult to detect if air aliquots smaller than 100 L are analyzed with GC/ECD or GC/MSD.

The use of CCSG as an alternative and more effective sampling material allowed a better discussion of the sampling efficiency on silica gel and the possible artifact formation during sampling. The 200 m³ of air was collected on CCSG simultaneously with a silica gel sample. The superiority of CCSG to silica gel can be summarized as follows: C_6–C_8 alkyl nitrates showed breakthrough and loss on silica gel at 15–20 °C when air volumes of >150 m³ were collected. Concentrations of these compounds could only be estimated in our earlier measurements (27). CCSG allowed quantitative high-volume sampling of $\geq C_6$ alkyl nitrates at the largest sampling volume in California (200 m³ at 17–18 °C). The breakthrough of C_6-, C_8-, and C_{10}-nitrates was 40%, 22%, and 15%, respectively, and was added to obtain the total amount. The silica gel sample showed a loss of 21% for all measured C_6–C_{12} alkyl nitrates as compared to the CCSG. The sampling volumes for all other silica gel samples collected in California were ≤ 150 m³ and should have an error due to sampling efficiency which is $\leq 20\%$. Artifact formation of alkyl nitrates on the sampling material seems unlikely since equal results are obtained using silica gel or CCSG.

In this and earlier work (26), the particle phase was analyzed by liquid extraction of the glass fiber filter and GC analysis. Long-chain alkyl nitrates adsorbed on particles
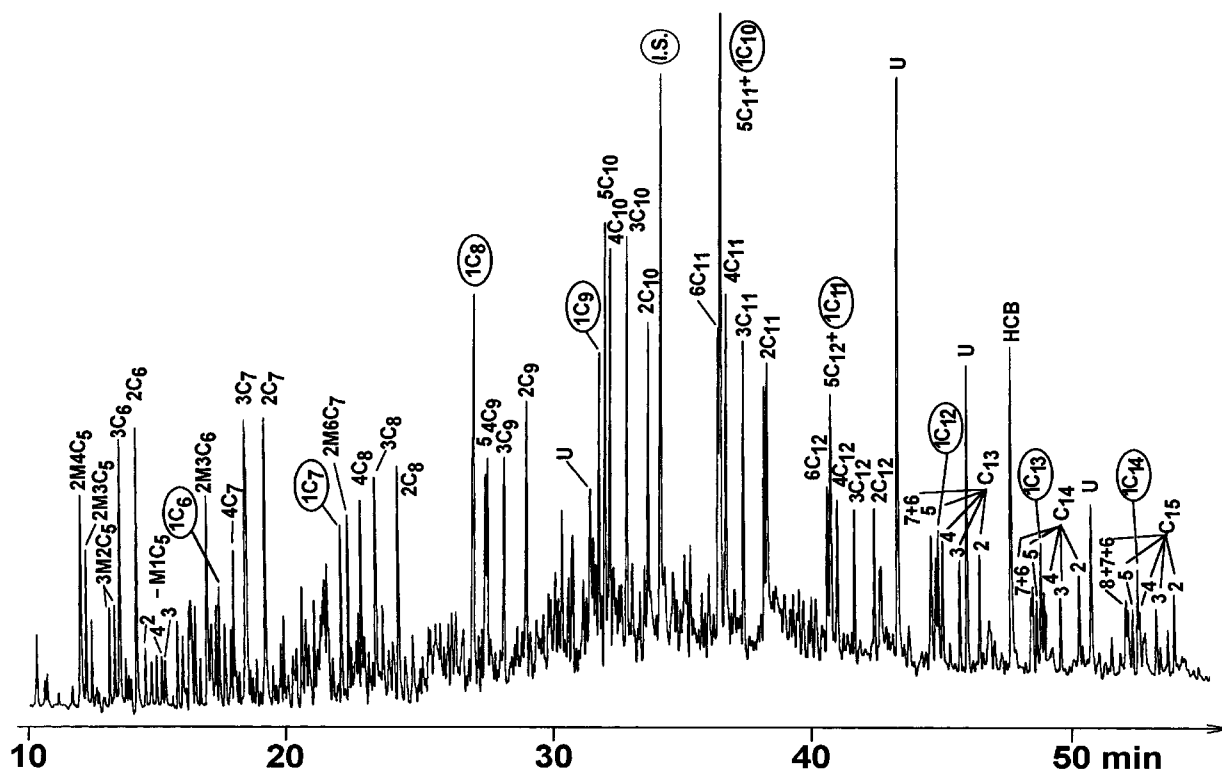
FIGURE 2. HRGC(DB1)/ECD (LC fraction 1b): Selective detection of C_6-C_{15} alkyl nitrates in marine air (1900 L aliquot) at the California Coast. The primary n-alkyl nitrates $1C_6-1C_{14}$ are marked. HCB, hexachlorobenzene.

could not be detected in any samples. To explain this, we determined the vapor pressures of approximately 80 alkyl nitrates and dinitrates. The relevant vapor pressures up to n-C_{21}-alkyl nitrates are published (*26*). The vapor pressures of $1,3C_3-1,8C_8$-dinitrates are determined to range from 7.2 $\times$ 10^{-1} 1.1 $\times$ 10^{-3} Torr (298 K). Using these values, the isothermal gas-to-particle ratio can be calculated with the Junge equation (*31*). We calculated for urban conditions that the particle adsorption of alkyl nitrates and dinitrates up to C_{16} and C_8, respectively, is less than 1% and therefore not significant. In marine air, the gas-to-particle ratio is even more shifted in favor of the gas phase because the particle surface is significantly lower. In general, the same conclusions are drawn by Nielsen et al., who suggest that future work should focus on the development of methods to determine the possible presence of gas-phase bifunctional organic nitrates because the fraction of particulate organic nitrate was determined to represent only 0.25% of total NO_y (*32*).

Mass Spectral Properties of Alkyl Dinitrates and Aromatic Nitrates. Positive EI− as well as negative CI−MS detection of alkyl nitrates in air samples has been reported (*13, 20, 21*). All systems take advantage of the specific [NO_2] fragment (m/e 46). However, we find that m/e 46 is not the most abundant fragment in the EI mode for >C_4-nitrates. Besides the alkyl chain fragments, the EI mass spectra of alkyl nitrates show a further fragment based on the carbon− carbon bond cleavage in vicinity of the −ONO_2 group (α-cleavage). The mass of this fragment is specific for the position x of the −ONO_2 group and can therefore be used for an isomer-specific determination of alkyl nitrates. This general "position-selective" fragment for a $x-C_n$ alkyl nitrate is [$C_xH_{2x}ONO_2$]$^+$, e.g., the mass spectra of the position isomers of the n-nonyl nitrates show fragments of m/e = 132, 118, 104, 90, and 76 for the 5-, 4-, 3-, 2-, and 1-C_9 nitrate, respectively. Results for the mass spectra of the synthesized dinitrates are similar. In this case, m/e 46 is always the most abundant fragment followed by the described position-

selective fragments, e.g., $1,2C_3$-dinitrate shows 46, 76, and 90 m/e 100/22/8% (relative abundance). The EI mass spectra of benzyl nitrate and the o-, m-, and p-methylbenzyl nitrates show the molecular ion [M]$^+$ and the characteristic fragments of aromatic compounds. The most significant ions useful for air sample analysis of benzyl- and the methylbenzyl nitrates are [M]$^+$/[C_6H_5]$^+$/[NO_2]$^+$ = 153/77/46 m/e = 14/ 100/7% and [M]$^+$/[$CH_3C_6H_5$]$^+$/[NO_2]$^+$ = 167/91/46 m/e = 28/100/14%, respectively.

Air Mass Characterization using C_2Cl_4 and $CHBr_3$ as Tracers. The air samples taken at the California coast (Meteorological Station) could not be distinguished from those taken on the RV *Shana Rae*. Together, they represent the concentrations measured in marine air at Santa Cruz, CA (Table 1). C_2Cl_4 and $CHBr_3$ mixing ratios unequivocally justify the classification of the air samples taken in the coastal mountains at Boulder Creek, CA, into the Northern Hemispheric (NH) continental group. The anthropogenic marker C_2Cl_4 is five times less abundant in the Santa Cruz samples as compared to the air in the coastal mountains. Furthermore, our data suggest a chronological decrease of C_2Cl_4 observable in marine regions within 1982 and 1995 (Table 1 and refs *15, 16,* and *33−36*). Supported by the following arguments, we think that seasonal or latitudinal variations most likely cannot account alone for this decrease. Interhemispheric comparison of C_2Cl_4 concentrations shows a mean NH/SH ratio of 3 (= 15 pptv/5 pptv). This value represents a global overall average (all seasons) of several measurements carried out between 1982 and 1985 (*34, 36*). Our results give a contemporary marine NH− (36° N, Santa Cruz) to SH− (35−40° S; Atlantic westwind belt) ratio for C_2Cl_4 of 2.6 (= 2.1 pptv/0.8 pptv). Thus, the concentrations of C_2Cl_4 in the marine Northern and Southern Hemispheric troposphere decreased 7-fold in the last 10 years without a significant change in the NH/SH ratio. All measurements were carried out either in summer or fall. Seasonal variations, which could bias this ratio, are of minor relevance because we compare only less polluted marine air away from emission

TABLE 1. California Measurements of C_3-C_{12} Alkyl Nitrates and Selected Halocarbons (in ppt v) and Global Atmospheric Comparison

	ΣC_3	$\Sigma C_4 + C_5$	$\Sigma C_3 - C_5$	$\Sigma n/i C_6 - C_{12}$	$\Sigma n/i C_3 - C_{12}$	C_2Cl_4	$CHBr_3$	ref
NH, Continental								
Boulder Creek, CA 1995	20.3	17.7[a]	38.0[a]	15.9	53.9	11.9	0.7	this work
Ulm 1993/95	17.6	23.4[a]	61.0[a]	13.6	74.6			20, 27
Nova Scotia 1993	10−50[b]							23
Alaska 1993			34.0[c]					24
Kinterbish, AL 1992			52.0[d]					22
Ontario 1992			53[a,e]					11
Scotia, PA 1988			72.0					22
Jülich 1988	27.4	69.3	96.7					14
Arctic, Kanada 1988			141.0[f]					18
NH, Marine								
Santa Cruz, CA 1995	9.6	7.4[a]	17.0[a]	2.3	19.3	2.1	2.3	this work
Pacific 1990	6.2	3.8	10.0			4.5	1.8	16
Hawaii 1988	2.6	2.4	5.0			4.7	0.3	15
Pacific 1987		3.0				12.0	1.0	15
Pacific 1986		9.0				15.0	0.9	13, 15
Atlantic 1985						15.0	2.0	33, 34
SH, Marine								
Atlantic trade winds 1994	1.3	1.6[a]	2.9[a]	0.6	3.5	0.6	0.7	27, this work
Atlantic west winds 1994	5.0	3.4[a]	8.4[a]	2.7	11.1	0.8	0.8	27, this work
Africa Coast 1990	9.2	8.6	17.8					19
Pacific 1987		0.6						15
Atlantic 1985						5	1.0	35, 36

[a] Includes isonitrates 2M1C3, 2M3C4, 2M4C4. [b] $\Sigma C_1 - C_4$. [c] $\Sigma C_2 - C_6$. [d] $\Sigma C_2 - C_5$. [e] $\Sigma C_3 - C_6$. [f] $\Sigma C_3 - C_7$.

sources and because it is known that C_2Cl_4 concentrations peak in wintertime clearly due to lower levels of hydroxyl radicals (37). Moreover, Wang et al. showed that seasonal variations of C_2Cl_4 are not significant in the Southern Hemisphere. Their measurements in late summer 1989 are in very good agreement with our results here because their average NH C_2Cl_4 concentrations of less than 10 pptv and SH concentrations of 1−2 pptv give a NH/SH ratio of ≈ 5 (37).

A further internal control of our measurement is provided by $CHBr_3$, which should not change over time like C_2Cl_4. $CHBr_3$, as a marine-biogenic marker molecule (33, 35), is three times more abundant at the California coast as compared to the concentrations inland. 2.3 pptv is a typical concentration for a coastal region with a high occurrence of macro algae, the primary production source of $CHBr_3$. As also shown in Table 1, mixing ratios of $CHBr_3$ in the marine troposphere away from the coast are typically lower (33, 35).

C_3-C_{12} Alkyl Nitrate Concentrations in California and Global Comparison. The average daily concentrations of $\Sigma n/i$-C_3-C_{12} alkyl nitrates [approximately 100 single compounds in Figures 1 and 2 (27)] at the California coast (19.3 pptv) are a factor of 3 lower than those measured inland (53.9 pptv). The coastal levels are even 7 times lower if only the long-chain $\Sigma n/i$-C_6-C_{12} alkyl nitrates are compared. As already discussed, the atmospheric lifetimes of alkyl nitrates decrease with the chain length because of increasing OH reaction (5, 6). Assuming transport (or storage) and degradation of alkyl nitrates in nonpolluted areas, the concentrations of alkyl nitrates must decrease faster with increasing alkyl chain. Thus, the levels of alkyl nitrates at the coast (Santa Cruz) represent air masses after transport from the central North Pacific region. The available meteorological data also show long-range transport of the air masses in the Pacific westwind drift but cannot characterize the ultimate source. Atlas found good correlation with radon for the first measurements of short-chain alkyl nitrates in the mid-Pacific region and also suggested long-range transport (13).

The California data allow the first global comparison of the whole range of $\Sigma n/i$-C_3-C_{12} alkyl nitrates (Table 1). The first measurements in the 1980s cover only $\leq C_5$ short-chain alkyl nitrates. Iso-alkyl nitrates were not always determined

in the previous investigations. This crucial fact is considered in Table 1 (footnotes) as accurate as possible. The average NH continental levels are satisfactorily studied up to the pentyl nitrates (11, 20, 22−24). Approximately 40−60 pptv are measured for ΣC_3-C_5 alkyl nitrates in rural regions. Urban concentrations can be twice as high (14). Short-chain $<C_8$ alkyl nitrates are known to contribute a fraction of 2−5% to total NO_y (23 and references therein). This fraction can increase up to 20% during the Arctic spring (18). Our measurements of long-chain alkyl nitrates in rural areas, including the iso-nitrates (Boulder Creek, CA, and Ulm: $\Sigma n/iC_6-C_{12} = 14.5$ pptv), show that these compounds contribute with a fraction of 30% to all $\Sigma n/i$-C_3-C_{12} alkyl nitrates. Consequently, the continental long-chain alkyl nitrates $\geq C_6$ in the gas-phase contribute an additional 1−2% to the total NO_y. This is 1 order of magnitude more than the fraction of particulate organic nitrate (32).

The NH mixing ratios of all alkyl nitrate measurements in marine air are generally lower than those in NH continental air. The results in Santa Cruz do not show significant changes as compared to earlier measurements (15, 16). The obtained marine levels of C_3-C_5 alkyl nitrates (17.0 pptv) are not different from measurements of 10 or 5 pptv in the Pacific troposphere because additional iso-alkyl nitrates are included in the Santa Cruz measurements.

Interhemispheric comparison shows that levels of C_3-C_5 alkyl nitrates in marine air in California are in the same concentration range as those determined by deKock et al. at the South African coast (19). They are also comparable to the average concentrations of short- and long-chain alkyl nitrates in the South Atlantic westwind drift (27). The lowest levels of alkyl nitrates have been determined in the South Pacific (0.6 pptv) (15) and the trade wind region of the South Atlantic ($C_3-C_{12} = 3.5$ pptv) (27). Again, both results represent a similar absolute concentration because of the higher number of single alkyl nitrates measured in the latter case. The determined data sets of alkyl nitrates in California and in the South Atlantic extend the knowledge of the global contribution of short- and long-chain alkyl nitrates. The concentrations determined for the marker halocarbons C_2-Cl_4 and $CHBr_3$ are consistent with the literature and confirm
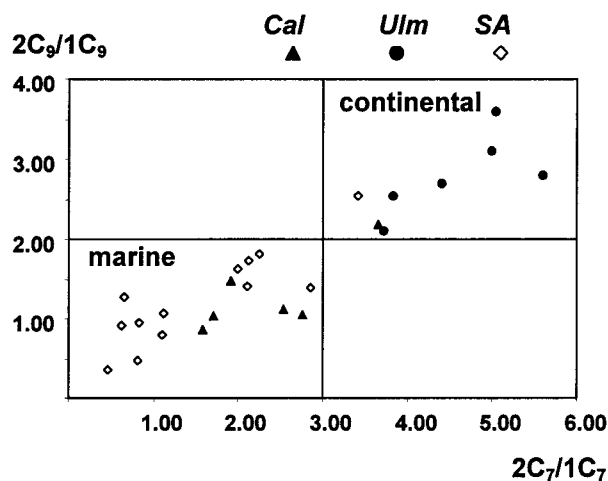
FIGURE 3. Correlation of secondary/primary n-heptyl- and n-nonyl nitrates leads to a spatial clustering of the continental and marine air samples in California. Results obtained in central Europe and the South Atlantic region are included (27). Cal, California samples; Ulm, continental air samples from Ulm, Germany; SA, South Atlantic air samples.

correct air sampling and analysis. This is a critical issue if field measurements are discussed because they often result from single expeditions leading to unique sample material. The 1994 South Atlantic halocarbon data are reported here for the first time. The additional interhemispheric comparison of C_2Cl_4 and $CHBr_3$ shows how important the global alkyl nitrate measurements can be for the future. The data can be assessed in a similar way with continuing measurements and they are accessible for model calculations, e.g., the relevance of organic nitrates in tropospheric ozone formation (13).

Global Pattern Analysis with Primary and Secondary Alkyl Nitrates. The common characteristics of the chro-

matograms (see also above) have been discussed (27), e.g., the influence of odd and even carbon numbers on the abundance of isomeric secondary n-alkyl nitrates. In general, all samples have very similar chromatographic patterns of alkyl nitrates. Primary n-alkyl nitrates make an important exception. In consonance with their lower photochemical formation yields (4), we find 3–10-fold lower abundance of primary long-chain n-alkyl nitrates ($1C_6 - 1C_{14}$) in continental air as compared to secondary alkyl nitrates (27). The primary long-chain alkyl nitrates are of increased intensity in the marine air samples as can be seen in Figure 2. Figure 3 depicts the correlation of the ratios of secondary to primary heptyl and nonyl nitrates. The previous results of air samples from central Europe (Ulm, Germany) and from the remote South Atlantic region are included (27). These air samples are clearly characterized as continental and marine, respectively. One California air sample and one air sample from the South Atlantic region show a continental-like pattern in Figure 3. The first was collected 25 mil away from the California coast in Boulder Creek and the latter in the westwind belt close to South America, respectively.

There are different possibilities that would explain increased primary alkyl nitrates in marine air. First, photolysis of primary long-chain alkyl nitrates could be slower than for the secondary nitrates. Second, long-chain aldehydes could serve as a possible source for primary nitrates via photolysis or via peroxyacyl nitrates as intermediates and subsequent unimolecular decomposition to the C_{n-1}-primary nitrate (27). We favor the latter hypothesis because it is in agreement with thermal decomposition studies of long-chain peroxyacyl nitrates (38) and with new results reported on the simulation of the photooxidation of n-alkanes under marine-environmental conditions (39). In the latter study, 1-alkenes and n-aldehydes could be detected as photooxidation products of $>C_{12}$ n-alkanes. The correlation described here is a further example for the application of alkyl nitrate data. Alkyl nitrates have already been shown to be useful as
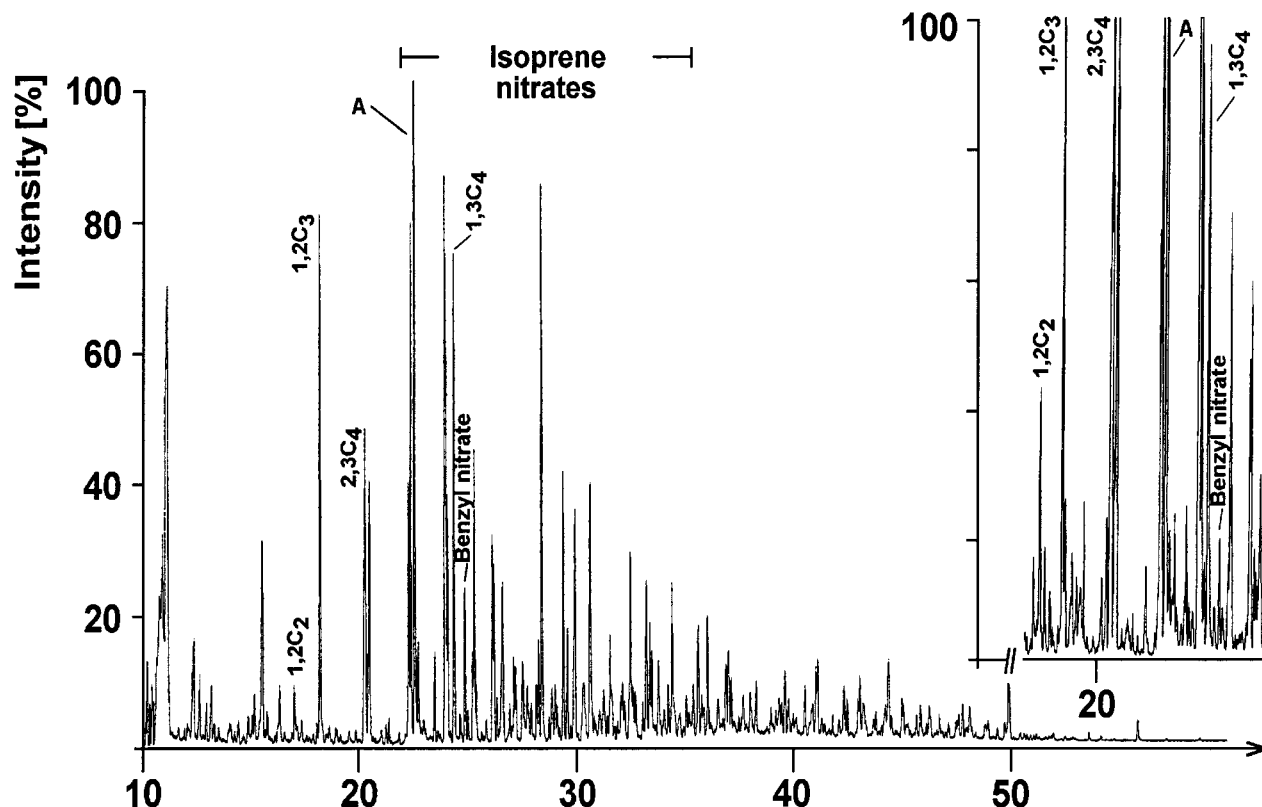

FIGURE 4. HRGC(CP−Sil2)/MSD (LC fraction 2): Selective detection (m/e 46) of alkyl dinitrates and benzyl nitrate in a daytime air sample (Ulm, Germany). The partial chromatogram shows the same air aliquot for a nighttime sample (1200 L).

TABLE 2. Global Relative Abundance of 4C$_8$-Nitrate and Benzyl Nitrate (BzN)

sampling site	region	4C$_8$/BzN
Boulder Creek, CA 1995	NH, rural	0.4
Ulm, Germany 1995	NH, rural	0.4
Santa Cruz, CA 1995	NH, marine	1.5
Atlantic, west wind 1994	SH, marine	3.7
Atlantic, trade wind 1994	SH, marine	5.3

air tracers because of their good correlation with ozone and other compounds (*11, 22−24*).

Alkyl Dinitrates and Benzyl Nitrate in Air Samples—Use as Tracer Molecules. We analyzed LC fraction 2 of high volume air samples from California, the South Atlantic, and central Europe (Table 2) monitoring *m/e* 46 and the isomer-selective ions described above. Figure 4 shows the SIM−MS detection obtained for *m/e* 46 from a daytime air sample collected in Ulm (Germany). The chromatogram shows the abundance of numerous polar organic nitrates in the same GC retention range as the alkyl mononitrates (compare Figure 2). We chose to show this sample because a comparable nighttime sample was also available (see sample locations and weather conditions). Generally, the daytime samples show very similar chromatographic patterns. The significant part of the nighttime sample is also shown in Figure 4. Proof of detection of the assigned dinitrate peaks and of benzyl nitrate is explained as follows. The synthesized reference compounds elute in the same LC preseparation fraction and have the same GC retention time. All depicted C$_2$−C$_4$-dinitrate peaks show (besides the most abundant [NO$_2$]$^+$ fragment) the position-selective fragments described above. The detected benzyl nitrate has the same relative abundance of the ions [M]$^+$/[C$_6$H$_5$]$^+$/[NO$_2$]$^+$ as observed in the reference mass spectrum. The methylbenzyl nitrate isomers, also available as reference compounds, could not be detected in any air sample. Although we do not have the reference compound, our analysis suggests that the peak labeled with A represents 1,2-dinitrooxybutane (1,2C$_4$-dinitrate).

The first pattern analysis of the polar organic nitrate fraction 2 revealed three important results. First, there is an obvious difference in the daytime and nighttime abundance of the vicinal alkyl dinitrates. These compounds are mainly products of alkene/NO$_3$ nighttime reactions (see Introduction). The nighttime sample shows significantly higher abundance for vicinal dinitrates as compared to the daytime sample (equal air aliquots analyzed). Benzyl nitrate and 1,-3C$_4$-dinitrate, as typical products of OH/NO daytime chemistry, do not follow the same trend. This could be expected but has never been shown. Second, because of its aromatic properties, the atmospheric removal processes of benzyl nitrate must be different than those of alkyl mononitrates. Table 2 shows the relative abundance of 4C$_8$-nitrate and benzyl nitrate in air samples from different regions (4C$_8$ was chosen to represent the alkyl mononitrates because it is in the "center" of the C$_3$−C$_{12}$ nitrates). The relative ratios of 4-octyl nitrate and benzyl nitrate (4C$_8$/BzN) were obtained by consecutive injections of the LC preseparation fractions 1b and 2. Using the ECD, the internal standard heptachloropropane allowed the comparison of identical air aliquots with no injection error. The values indicate that these compounds have a different atmospheric behavior. The relative amount of benzyl nitrate is lower in marine air as compared to continental air, which is not surprising since the highest concentrations for benzyl nitrate can be expected in urban areas due to its precursor toluene (traffic emissions). The results in the South Atlantic could indicate an inter-hemispheric difference (as shown above for the tracer molecule perchloroethylene). However, these results stand alone and have to be confirmed yet. Third, it is likely that our sampling technique may be useful for the analysis of hydroxy nitrates deriving from isoprene [commonly named isoprene nitrates (*8, 11*)]. Retention index calculations (*30*) allow an estimate of the retention times for the isoprene nitrates. The time range where isoprene nitrates elute is indicated in Figure 4. The mass selective detection in combination with the preseparation provides good evidence that several peaks in this range represent isomers of the isoprene nitrates and other similar organic nitrates (*9, 40*).

Nomenclature of Alkyl Dinitrates and Bifunctional Organic Nitrates

In the IUPAC nomenclature, the −ONO$_2$ group is called nitro-oxy group. We have suggested a shorthand nomenclature structure related to the hydrocarbon precursor of alkyl mononitrates to characterize a single compound in complex mixtures, e.g., 2,4M5C$_8$ nitrate is the 2,4-dimethyl-5-nitrooxyoctane (*30*). This can be extended to bifunctional nitrates. In the case of branched alkyl nitrates, the alkyl side chains are given higher priority than the nitrooxy group. The same holds for the keto and the hydroxy group, which are given a higher priority than the nitrooxy group but lower than the alkyl side chains. Keto groups are indicated as (O) and hydroxy groups as (OH). As a general example, the abbreviations 2M3,4C$_5$ and 2(OH)3C$_4$ are given indicating the dinitrate 2-methyl-3,4-dinitrooxypentane and 2-hydroxy-3-nitrooxybutane, respectively. This convention is helpful if isomeric hydrocarbon skeletons have to be distinguished. If the nitrooxy group would be given higher priority than the alkyl side chains, closely related isomeric nitrates would be named different.

Acknowledgments

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