

# Separation, detection and occurrence of (C2–C8)-alkyl- and phenyl-alkyl nitrates as trace compounds in clean and polluted air

Oliver Luxenhofer, Ellen Schneider, Karlheinz Ballschmiter

Department of Analytical and Environmental Chemistry, University of Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

Received: 4 October 1993 / Accepted: 25 January 1994

**Abstract.** Nitric acid,  $\text{HNO}_3$ , and nitrous acid,  $\text{HNO}_2$ , are forming stable esters with alcohols, the alkyl nitrates and alkyl nitrites. Both groups of compounds are used as fuel additives, explosives and pharmaceuticals. Alkyl nitrates are also formed as complex mixtures during incomplete combustion and the abiotic transformation of alkanes, alkenes and aldehydes in air. Organic nitrates can be assigned to anthropogenic and natural sources alike. Here the synthesis of reference mixtures of alkyl nitrates is described starting with alcohols, alkyl bromides, alkyl iodides or alkanes, respectively, sampling techniques in air analysis, and the separation of alkyl nitrates and alkyl dinitrates by high resolution capillary gas chromatography using various stationary phases and electron capture (HRGC/ECD) as well as mass spectrometric detection (HRGC/MSD). A highly selective detection mode for alkyl nitrates and alkyl di- and trinitrates – in general in the presence of other organic trace compounds – is the single ion monitoring of 46 amu in GC/MS. The separation and occurrence of alkyl- and phenyl-alkyl nitrates in polluted air is reported using capillary gas chromatography with electron capture and ion trap MS detection. The reaction of alkanes with nitric acid at room temperature simulates in a good approximation the pattern of alkyl nitrates formed in air chemistry.

## 1 Introduction

Nitric acid,  $\text{HNO}_3$ , forms with alcohols stable esters, the alkyl nitrates. The C- $\text{ONO}_2$  moiety as a second functional group in a molecule is called nitroxy-group. Nitrous acid,  $\text{HNO}_2$ , also forms stable esters with alcohols, the alkyl nitrites. Both groups of compounds are used as Diesel fuel additives, explosives [1] and pharmaceuticals. Isosorbide dinitrate is a powerful vasodilator. Alkyl nitrates are formed during combustion and in air as well [2]. They are environmental chemicals with both natural

and anthropogenic sources. Organic nitrates are present in the remote troposphere [3].

The formation of alkyl nitrates in air is mainly governed by the stability of the parent alkyl radical  $\text{R}^*$ . Alkyl radicals are formed by the reaction of  $^*\text{OH}$  radicals with hydrocarbons and by the photolysis of aldehydes. The latter photolyse to  $\text{R}^*$  and  $\text{HCO}^*$ . The  $\text{HCO}^*$  radical reacts with  $\text{O}_2$  to CO and  $\text{HO}_2^*$ . The reaction rate of alkanes with  $^*\text{OH}$  radicals to form water and  $\text{R}^*$  radicals increases with the chain length of the hydrocarbon [4, 5, 6, 7]. Branching of the chain increases the probability of a hydrogen subtraction due to the increased stability of the alkyl radical formed. Alkyl radicals with or without a second functional group can also derive from the addition of  $^*\text{OH}$  or  $\text{NO}_3^*$  radicals to olefins especially to the biogenically important isoprenes, terpenes and low molecular alkenes [8, 9, 10]. Hatakeyama presented in this context a very detailed photochemical reaction model for the propene- $\text{NO}_x$ -air system [11]. The alkyl radical  $\text{R}^*$  reacts immediately with oxygen to the corresponding alkyl peroxy radical  $\text{RO}_2^*$ . The alkyl peroxy radical  $\text{RO}_2^*$  reacts in the presence of NO – which itself forms  $\text{NO}_2$  – to the alkoxy radical  $\text{RO}^*$ . NO can also be added to  $\text{RO}_2^*$  in a side reaction forming the alkyl nitrates (Fig. 1) [4, 12]. The formation of alkyl nitrates becomes with increasing chain length of the alkyl peroxy radical [6] a dominant reaction.

Organic peroxy radicals  $\text{RO}_2^*$  may react among themselves at rates which can compete for reactions with NO and  $\text{HO}_2^*$  particularly under conditions of low NO/ $\text{NO}_2$  concentrations as encountered in the clean marine atmosphere [13]. Simulation of effects of such self-reactions (permutation reaction) of organic peroxy radicals in clean air leads to higher  $\text{HO}_2^*$  and  $\text{H}_2\text{O}_2$  concentrations, shorter lifetimes for peroxyacyl nitrates (PAN) with the result of a faster release of  $\text{NO}_2$  and the production of increased concentrations of alcohols and organic acids. Increased levels of  $\text{NO}_2$  lead by photolysis to increased levels of NO which by reaction with an alkyl peroxy radical may stabilise as a nitrate.

Reaction of alkyl peroxy radicals  $\text{RO}_2^*$  with  $\text{NO}_2$  in the presence of a third inert collision partner leads to

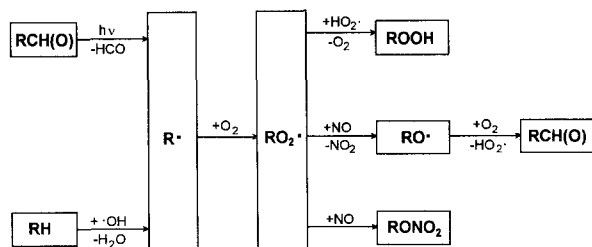


Fig. 1. Reaction pathways of alkyl nitrate formation from alkanes and aldehydes in air chemistry:  $R = C_nH_{2n+1}$ , phenyl- $(C_nH_{2n})_n$ , naphthyl- $(C_nH_{2n})_n$

alkyl peroxy nitrates,  $ROONO_2$ . Synthesis and thermal stability of this group of nitrous pollutants has been summarised by Edney et al. [14, 15]. The stability of the peroxy nitrates increases substantially when the peroxy group carrying carbon is substituted by chlorine and/or fluorine,  $R-C(F,Cl)OONO_2$ . The chlorofluoromethyl-peroxy nitrate,  $ClFCOONO_2$ , is about as stable as the well known peroxyacetyl nitrate (PAN),  $CH_3C(O)OONO_2$ .

The occurrence of short chain alkyl nitrates in polluted atmosphere has been known for long [16]. We report here on the analytical chemistry of C1–C8-alkyl nitrates and aryl-alkyl nitrates in general in the environmental compartment atmosphere. The procedures described can be easily extended to long chain alkyl nitrates with carbon numbers up to 30 and to bifunctional nitrates as well.

## 2 Experimental

### 2.1 Instrumentation

#### 2.1.1 Gas chromatography

Gas chromatograph: Chrompack CP 9001 thermal desorption unit/Electron capture detector: 260 °C  
HP 5890 II/Electron capture detector: 260 °C

#### 2.1.2 Gas chromatography/Mass spectrometry

Varian Saturn MS II Ion Trap detector

#### 2.1.3 Capillary gas chromatography

Methyl-octadecyl (50%) polysiloxane, (Chrompack) length: 105 m; i.d.: 0.32 mm; film thickness: 0.25  $\mu$ m; injector: 260 °C splitless, He, Temp.: 40 °C (3 min)-4 °C/min-180 °C (3 min)

CP Sil 8 (Chrompack), length: 50 m; i.d.: 0.25 mm; film thickness: 0.25  $\mu$ m; injector: on column, He, Temp.: 40 °C (3 min)-3 °C/min-250 °C

CP Sil 13 (Chrompack), length: 50 m; i.d.: 0.34 mm; film thickness: 1.2  $\mu$ m; injector: 250 °C splitless, He, Temp.: 40 °C (10 min)-4 °C/min-260 °C (3 min)

DB 1701 (J&W), length: 60 m; i.d.: 0.32 mm; film thickness: 1  $\mu$ m; injector: 175 °C splitless,  $N_2$ , Temp.: 40 °C (3 min)-3 °C/min-190 °C

Table 1. Structure and systematic numbering of C1–C6 alkyl nitrates and alkyl nitrites. The systematic numbering is used as a structure defined synonym for the single compounds. This general approach of structuring complex mixtures of correlated compounds has been widely accepted for the PCB and other complex mixtures

|                                     |    |                           |
|-------------------------------------|----|---------------------------|
| C1-ONO/-ONO <sub>2</sub>            | 14 | 2-Methyl-3-butyl-         |
| 1 Methyl-                           | 15 | 2-Methyl-4-butyl-         |
|                                     | 16 | 2,2-Dimethyl-1-propyl     |
| C2-ONO/-ONO <sub>2</sub>            |    | C6-ONO/-ONO <sub>2</sub>  |
| 2 Ethyl-                            |    | 17 1-Hexyl-               |
|                                     |    | 18 2-Hexyl-               |
| C3-ONO/-ONO <sub>2</sub>            |    | 19 3-Hexyl-               |
| 3 1-Propyl-                         |    | 20 2-Methyl-1-pentyl-     |
| 4 2-Propyl-                         |    | 21 2-Methyl-2-pentyl-     |
|                                     |    | 22 2-Methyl-3-pentyl-     |
| C4-ONO/ONO <sub>2</sub>             |    | 23 2-Methyl-4-pentyl-     |
| 5 1-Butyl-                          |    | 24 2-Methyl-5-pentyl-     |
| 6 2-Butyl-(sek. Butyl)              |    | 25 3-Methyl-1-pentyl-     |
| 7 2-Methyl-1-propyl-(i-Butyl)       |    | 26 3-Methyl-2-pentyl-     |
| 8 1,1-Dimethyl-1-ethyl-(tert-Butyl) |    | 27 3-Methyl-3-pentyl-     |
|                                     |    | 28 2,2'-Dimethyl-1-butyl- |
| C5-ONO/-ONO <sub>2</sub>            |    | 29 2,2'-Dimethyl-3-butyl- |
| 9 1-Pentyl-                         |    | 30 2,2'-Dimethyl-4-butyl- |
| 10 2-Pentyl-                        |    | 31 2,3-Dimethyl-1-butyl-  |
| 11 3-Pentyl-                        |    | 32 2,3-Dimethyl-2-butyl-  |
| 12 2-Methyl-1-butyl-                |    | 33 2-Ethyl-1-butyl-       |
| 13 2-Methyl-2-butyl-                |    |                           |

Lipodex C (Macherey Nagel), length: 25 m; i.d. 0.25 mm; film thickness: 0.25  $\mu$ m; injector: 250 °C splitless,  $H_2$ , Temp.: 40 °C (3 min)-5 °C/min-200 °C

### 2.2 Preparation of reference mixtures of alkyl nitrates and alkyl nitrites

The number and structure of the C1- to C6-alkyl nitrates are summarised in Table 1. The number of isomers increase rapidly beyond the hexyl nitrates; there already exist 39 heptyl nitrate isomers.

#### 2.2.1 Commercially available alkyl nitrates and alkyl nitrites

The following alkyl nitrates and alkyl nitrites can be obtained commercially:

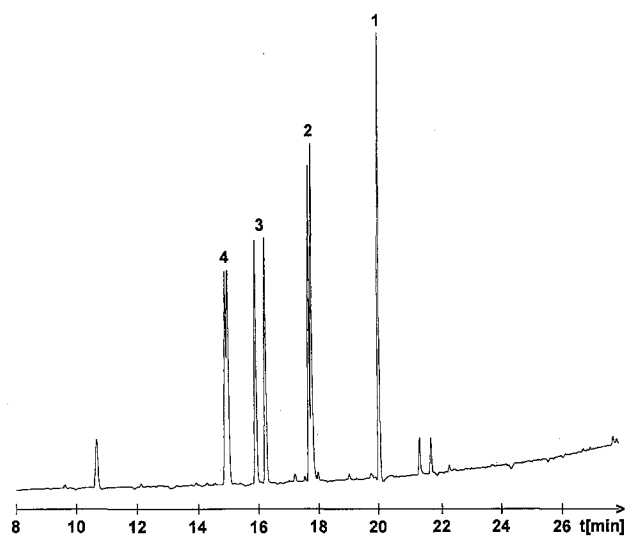
##### Alkyl nitrates

- 1-Propyl nitrate (Janssen)
- 2-Propyl nitrate (Aldrich)
- 2-Methyl-1-propyl nitrate (Aldrich)
- 2-Ethyl-1-butyl nitrate (Aldrich)
- 2-Ethyl-1-hexyl nitrate (Aldrich)

##### Alkyl nitrites

- Ethyl nitrite (Aldrich)
- 1-Butyl nitrite (Aldrich)
- 2-Methyl-1-propyl nitrite (Isobutyl nitrite) (Aldrich)
- tert. Butyl nitrite (Aldrich)
- 3-Methyl-1-butyl nitrite (Amyl-nitrite) (Aldrich)

Alkyl nitrates are normally synthesised in gram amounts or more by the reaction of an alcohol with concentrated nitric acid in the presence of urea [17, 18]. Larger amounts have to be handled with care. Some of the alkyl nitrates are used as explosives like other nitro-compounds [1]. Alternatively alkyl nitrates can be prepared as analytical reference mixtures by micro chemical techniques.



**Fig. 2.** HRGC (Lipodex C)/ECD gas chromatogram of an octyl nitrate-test mixture. Separation of chiral alkyl nitrates: 1: 1-Octyl nitrate (achiral), 2: 2-Octyl nitrate, 3: 3-Octyl nitrate, 4: 4-Octyl nitrate

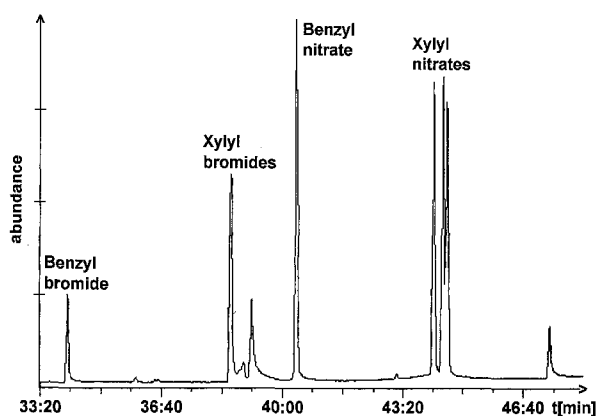
### 2.2.2 Microsynthesis with alcohols as precursors

Reference solutions in the microgram per millilitre range of alkyl nitrates are easily obtained by the reaction at room temperature of dilute solutions (4–10 mmol/l) of alcohols in a chlorinated hydrocarbon solvent preferably dichloromethane in contact with a mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (1:1), e.g. 5 ml solution of the alcohol in dichloromethane and 1 ml of the acid mixture. Reaction times of 30 min up to 5 h have been applied. Using a racemic alcohol results in pairs of nitrate enantiomers. Chirally defined alcohols lead to the corresponding chirally defined alkyl nitrates. Diols form the corresponding alkyl dinitrates.

This micro-technique which gives practically no interfering compounds in the electron capture detection has been used as a quick method to prepare a variety of single compounds and also mixtures of alkyl nitrates as reference standards for recording their retention characteristics in capillary gas chromatography with electron capture detection (HRGC/ECD). Separation of chiral alkyl nitrates is achieved by using perpentylated  $\beta$ -cyclodextrin coated capillaries (Lipodex C, Macherey & Nagel) (Fig. 2). Reaction of trichloroethanol leads to the nitrate of 1,1,1-trichloroethane, only to mention the flexibility of this reaction in making unusual organic trace compounds available.

### 2.2.3 Microsynthesis with alkyl bromides and alkyl iodides as precursors

Alkyl nitrates are also formed by the reaction of  $\text{AgNO}_3$  with alkyl bromides or aryl-alkyl bromides and with alkyl iodides or aryl-alkyl iodides [19, 20]. Silica gel covered with  $\text{AgNO}_3$  used in a column technique is a convenient approach to use the exchange reaction.  $\text{AgNO}_3$  is rather soluble in acetonitrile. The alkyl bromides and iodides were applied as neat substance in 2–10 mmol/l amounts



**Fig. 3.** HRGC (CP Sil13)/MSD full scan gas chromatogram of synthesis of phenyl-alkyl nitrates through the reaction of phenyl-alkyl-bromides with silver nitrate

to a solution of  $\text{AgNO}_3$  in acetonitrile. The drawback of the exchange reaction is that in most cases a reaction yield of only 60–80% is obtained even when  $\text{AgNO}_3$  is used in a substantial surplus and the reaction time is extended up to 20–30 h (Fig. 3).

A similar but fast and convenient modified exchange procedure has been used to get the alkyl nitrates as pure reference compounds. To a molar excess of  $\text{AgNO}_3$  dissolved in dried acetonitrile alkyl bromides or alkyl iodides dissolved in the same solvent were slowly added. After transferring the reaction mixture to ice water the alkyl nitrates were extracted two times with dichloromethane. The solvent was removed under reduced pressure to obtain the reaction products.

Alkyl nitrites,  $\text{RONO}$ , which can basically be obtained by a similar exchange reaction using alkyl bromides or iodides and  $\text{AgNO}_2$ , are even less readily formed. As further products among others the nitro-alkanes,  $\text{RNO}_2$ , are obtained [21].

### 2.2.4 Microsynthesis after halogenation of alkanes

The  $\cdot\text{OH}$  attack basically follows the same rules as it is known for the halogenation by  $\text{Cl}^*/\text{Br}^*/\text{I}^*$  radicals. Photosensitised bromination and iodization of alkane mixtures as n-pentane and n-hexane, n-heptane, lighter fuel (n-butane), petroleum-ether (bp. 30–60 °C), and gasoline and subsequent formation of the alkyl nitrates by reaction with  $\text{AgNO}_3$  leads to a complex spectrum of compounds. The 1-substituted nitrates are always only minor reaction products as the result of a less likely formation of the corresponding alkyl radicals. The halogens exhibit different reactivities which one can take advantage of. Bromination of alkanes in the dark also leads after the exchange with  $\text{AgNO}_3$  to a complex mixture of nitrates and further not yet identified compounds.

### 2.2.5 Microsynthesis with alkanes and aryl-alkanes as precursors

Titov has summarised in an extensive review the chemistry of nitration of alkanes and phenyl alkanes [22].

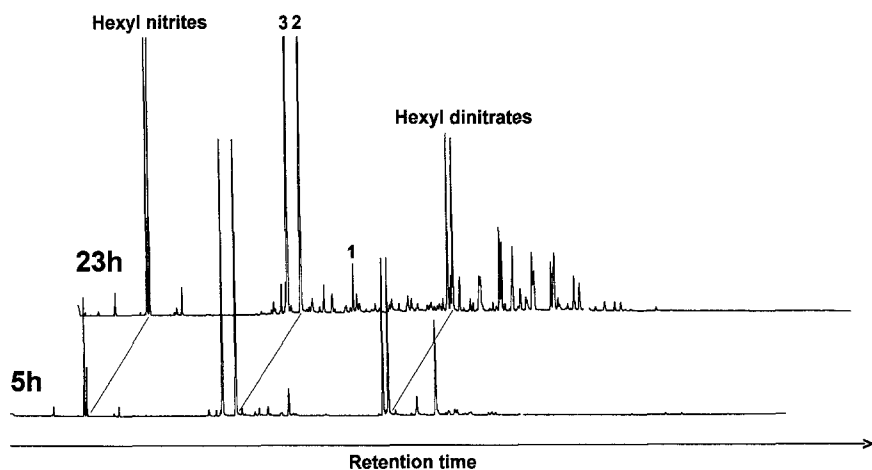


Fig. 4. HRGC (CP Sil8)/ECD gas chromatogram of the reaction mixture of hexane with 12%  $\text{HNO}_3$  and copper wire. 1: 1-Hexyl nitrate, 2: 2-Hexyl nitrate, 3: 3-Hexyl nitrate

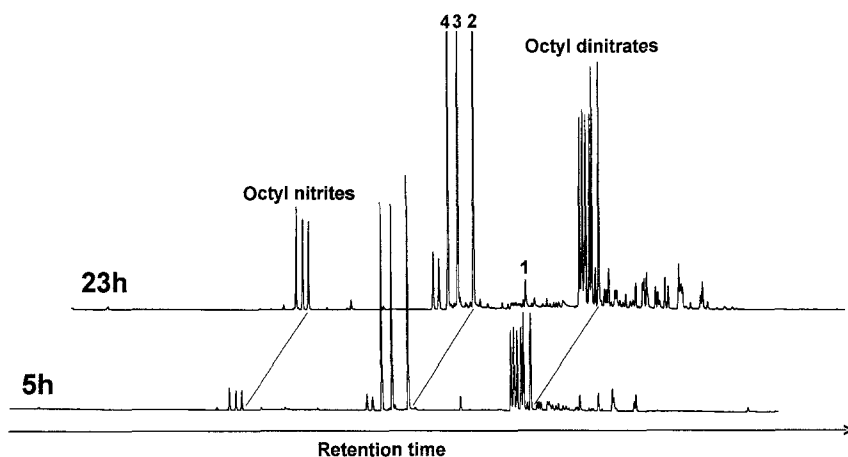


Fig. 5. HRGC (CP Sil8)/ECD gas chromatogram of the reaction mixture of octane with 12%  $\text{HNO}_3$  and copper wire. 1: 1-Octyl nitrate, 2: 2-Octyl nitrate, 3: 3-Octyl nitrate, 4: 4-Octyl nitrate

At room temperature the reaction of the alkanes at the solvent/nitric acid interface either involves peroxy radical formation leading to the alkyl nitrates or the active reagent are traces of  $\text{NO}_3^*$  which is stable at lower temperatures.

Neat hydrocarbons were let to react in a two-phase reaction with  $\text{NO}_x$ , which is formed by adding copper wire to a 12% solution of nitric acid. This simple reaction technique can be used for preparing predetermined complex mixtures of alkyl nitrates. We started with defined geogenic and biogenic alkanes, mixtures of alkanes or less defined alkane mixtures like petroleum-ether of the different boiling ranges, and various types of gasoline. The reaction products formed reflect the probability of the alkyl nitrate formation in the gas phase. Extending the reaction time from two hours at room temperature to about twenty hours and more leads to the additional formation of alkyl dinitrates and also to alkyl nitrites and alkyl dinitrites (Figs. 4–5).

Solutions of alkanes in dichloromethane do also react with  $\text{NO}_x$ . This reaction can lead to the formation of artifacts when cryosampling is used. The condensed  $\text{NO}/\text{NO}_2$  reacts rather fast with the extracting solvent if this is an alkane. The formation of interfering alkyl nitrates is easily detected in this case by changing the solvent (Figs. 6–7).

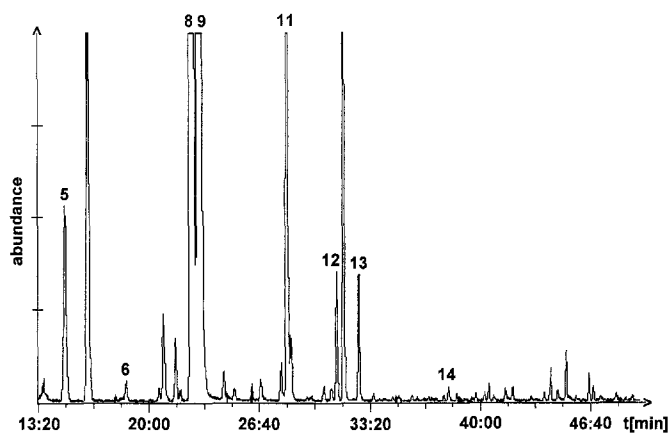
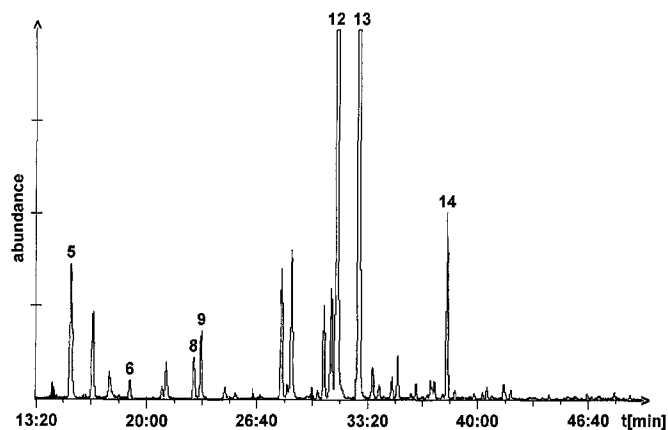


Fig. 6. HRGC (50%C18 + 50%CP Sil5)/MSD (amu 46) Cryogenic sampling of  $2.3 \text{ m}^3$  urban air through condensation at  $-196^\circ\text{C}$  using liquid nitrogen, followed by extraction of the condensate with pentane. 5: 2-Butyl nitrate + 2-Methyl-1-propyl nitrate, 6: 1-Butyl nitrate, 8: 3-Pentyl nitrate (artifact), 9: 2-Pentyl nitrate (artifact), 11: 1-Pentyl nitrate (artifact), 12: 3-Hexyl nitrate, 13: 2-Hexyl nitrate, 14: 1-Hexyl nitrate

### 2.3 Sampling of alkyl nitrates in air

The alkyl nitrates which can be expected in air extend in terms of sampling over both the volatiles and the



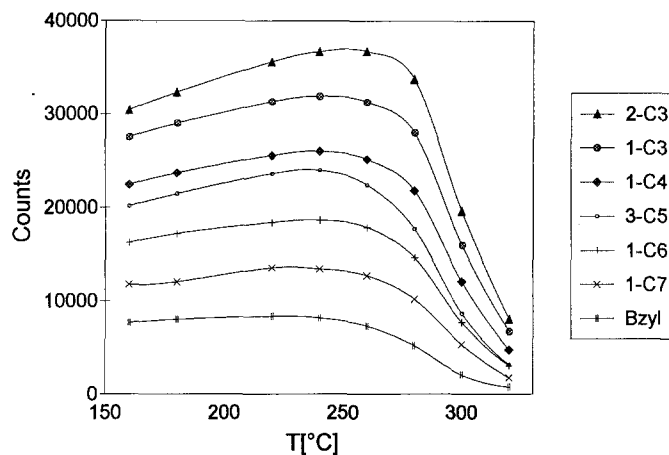
**Fig. 7.** HRGC (50%C18 + 50%CP Sil5)/MSD (amu 46) Cryogenic sampling of 3.1 m<sup>3</sup> urban air through condensation at -196 °C using liquid nitrogen, followed by extraction of the condensate with hexane. 5: 2-Butyl nitrate + 2-Methyl-1-propyl nitrate, 6: 1-Butyl nitrate, 8: 3-Pentyl nitrate, 9: 2-Pentyl nitrate, 12: 3-Hexyl nitrate (artefact), 13: 2-Hexyl nitrate (artefact), 14: 1-Hexyl nitrate (artefact),

semivolatiles as indicated by their boiling points (Table 2). According to the Junge equation [23], more than 99% alkyl nitrates up to C20 are in the gaseous phase even in urban air. The C1–C6 compounds are effectively sampled by adsorption on Tenax TA or Tenax TA/Carbopack B mixtures (5–30 l of air) followed by thermal desorbing injection into the gas chromatograph including cryofocussing [24, 25, 26]. The higher boiling alkyl- and aryl-alkyl nitrates are collected by high volume sampling (100–1000 m<sup>3</sup> of air) using pre-cleaned silica mixed with 2% of pre-cleaned Carbopack C as adsorbents. In this case Soxhlet extraction or solvent desorption, respectively, are used. Solvent desorption combines the advantages of using eluents with increasing eluotropic properties (e.g. pentane, dichloromethane, cyclohexane), multiple injections with various detection methods, and the possibility of pre-injection microchemistry.

Aliquots of at least 5–30 l of air have to be injected for capillary gas chromatography using electron capture detection when alkyl nitrates in the pptv or nanogram per m<sup>3</sup> range, respectively, have to be analyzed by a thermal desorption technique. Capillary gas chromatography requires either column temperatures below ambient or a phase ratio in the range of 200 to achieve the necessary retention of the methyl- and the ethylnitrate.

#### 2.4 Separation of alkyl nitrites and alkyl nitrates by capillary gas chromatography and electron capture detection

Solvent desorption after adsorption based sampling and on-column injection were mostly used prior to gas chromatography. When the splitless/split injection mode was used only a negligible dependence of signal height to injection port temperature was observed. Injection port temperatures of up to 190 °C can be afforded for the



**Fig. 8.** Relationship between the ECD-response of alkyl nitrates and the detector temperature

**Table 2.** Alkyl nitrates given in order of increasing boiling points. The retention in gas chromatography on a non-polar stationary phase like a methyl-octyl- or methyl-octadecyl-polysiloxane will follow the order of boiling points. The 1-n-alkyl nitrates are always the last eluting compounds of their carbon-number group. They can be used for window defining or as retention index marker

| Name                      | bp °C<br>(1013 Pa)   |
|---------------------------|----------------------|
| Methyl nitrate            | 64.6                 |
| Ethyl nitrate             | 87.2                 |
| 2-Propyl nitrate          | 101.7                |
| 1-Propyl nitrate          | 110                  |
| 2-Methyl-1-propyl nitrate | 123                  |
| 2-Butyl nitrate           | 124                  |
| 2-Pentyl nitrate          | 144                  |
| 3-Methyl-1-butyl nitrate  | 147–148              |
| 1-Pentyl nitrate          | 157                  |
| 1-Hexyl nitrate           | 171                  |
| 1-Heptyl nitrate          | ca. 215              |
| 1-Octyl nitrate           | ca. 240              |
| Cyclohexyl nitrate        | 181                  |
| Benzyl nitrate            | 101–104 <sup>a</sup> |
| p-Methyl-benzyl nitrate   | 115–118 <sup>a</sup> |
| 2-Nitroxy ethanol         | 75 <sup>b</sup>      |
| 3-Nitroxy-1-propanol      | 103–104 <sup>c</sup> |

<sup>a</sup> = 100 Pa, <sup>b</sup> = 50 Pa, <sup>c</sup> = 150 Pa

analysis of alkyl nitrites and alkyl nitrates with an optimum between 150 °C and 190 °C.

The electron capture detector gives a maximum, structurally and molar based response for the alkyl nitrates between temperatures of 220 °C and 260 °C (Fig. 8)

The separation of alkyl nitrate mixtures follows the order of the boiling points (Table 2). The new non-polar stationary phases like methyl-octyl-polysiloxane (Supelco) and methyl-octadecyl-polysiloxane (Chrom-pack) give superior separations for the alkyl nitrates. Chiral alkyl nitrates can be separated by cyclodextrin based stationary phases like Lipodex D (Macherey-Nagel) (Fig. 2). The respective order of boiling points for the alkyl nitrites are given in Table 3.

**Table 3.** Sequence of alkyl nitrites in the order of increasing boiling points. The retention in gas chromatography on a non-polar stationary phase like a methyl-octyl- or methyl-octadecyl-polysiloxane will follow the order of boiling points

|                                 | bp °C<br>(1013 Pa) |
|---------------------------------|--------------------|
| Methyl nitrite                  | -12                |
| Ethyl nitrite                   | 16.5               |
| 2-Propyl nitrite (i-Propyl)     | 4                  |
| 1-Propyl nitrite (n-Propyl)     | 49                 |
| tert. Butyl nitrite             | 63                 |
| Methyl nitrate                  | 64.4               |
| 2-Butyl nitrite                 | 68                 |
| 1-Butyl nitrite                 | 77.8               |
| Ethyl nitrate                   | 87.2               |
| 3-Methyl-butyl-1-nitrite        | 99.2               |
| 1-Pentyl nitrite (Amyl nitrite) | 104.5              |
| 1-Propyl nitrate                | 110                |
| 1-Hexyl nitrite                 | 129                |
| 1-Butyl nitrate                 | 135.5              |
| 1-Heptyl nitrite                | 156                |
| 1-Pentyl nitrate                | 157                |
| 1-Octyl nitrite                 | 174.4              |

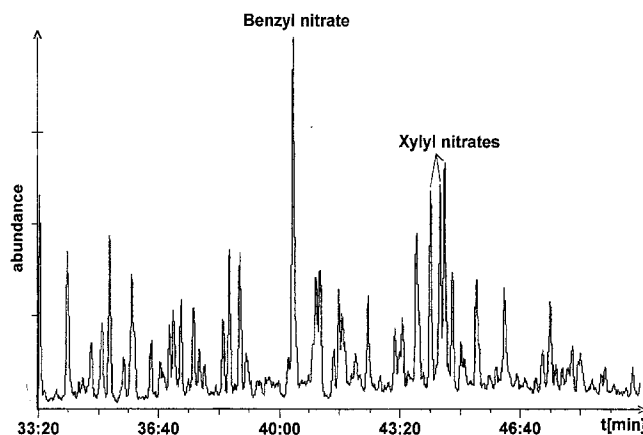
Phase selectivity is important for the separation of isomeric alkyl nitrates but is also needed to avoid overlapping of alkyl nitrates with other halogenated hydrocarbons particularly when an electron capture detector is used. In this respect the stationary phase OV 1701 is of advantage.

### 2.5 Detection of alkyl nitrates by mass spectroscopy at 46 amu

GC/MS is increasingly applied in organic trace analysis, since it combines in many cases both selectivity and sensitivity in detection. Combined with the separation power of capillary gas chromatography it is a technique with a high potential in the analytical chemistry of complex mixtures at trace levels.

For the analysis of alkyl nitrates by mass selective detection after electron impact (EI) ionization one can take advantage of the fragmentation pattern of the alkyl nitrates that leads to an extremely selective detection mode for alkyl nitrates. They form an intense 46 amu fragment ion that corresponds to  $\text{NO}_2^+$  [28, 29]. An ion of the mass 46 amu is rarely formed by any other combination of elements which renders this signal as specific for nitrates and other  $\text{NO}_2^+$  forming compounds. As a second indicator fragment the 76 amu ion corresponding to a  $\text{CH}_2\text{ONO}_2^+$  moiety is typical for n-alkyl nitrates. The alkyl nitrites give as typical fragments ions with 30 and 60 amu. Nitroalkanes do not form a 46 amu ion, the nitrophenols however give an ion of 46 amu of about 5% of the molecular ion. A weak 46 amu fragment is also observed for dinitrophenols, nitro- and dinitrocresols, and for pentachloronitrobenzene as well. A major fragment of 46 amu is observed for some urea herbicides like linuron or the superseded herbicides noruron.

Specificity for alkyl nitrates using the 46 amu trace in GC/MS can be obtained by a problem oriented



**Fig. 9.** HRGC (CP Sil13)/MSD (amu 46) gas chromatogram showing a time window of the chromatogram in Fig. 6

pre-separation of the sample solution. Such a pre-treatment of the sample solution using adsorption chromatography is easily done after high volume sampling and solvent desorption, it is less easily applied in a purge and trap injection technique.

Figures 6 and 7 depict the 46 amu trace obtained by ion trap GC/MS of two urban air samples collected in the vicinity of a parking lot by cryo-sampling with liquid nitrogen and extraction of the condensate with n-pentane and n-hexane, respectively.  $\text{NO}_x$  are also frozen out from air by cryo-sampling. NO has a boiling point of  $-151.8^\circ\text{C}$  while  $\text{NO}_2$  is boiling at  $21.2^\circ\text{C}$ . n-Pentane and n-hexane form their corresponding nitrates as interferences by the reaction with  $\text{NO}_x$  during sampling and sample preparation as discussed before. Using dichloromethane as the solvent avoids partly this interference. The reaction of the condensed hydrocarbons and the condensed  $\text{NO}_x$  during the sampling and storage of the extract is not excluded by this way. Cryo-sampling of nitrates needs the exclusion of the  $\text{NO}_x$  by a suitable absorption technique.

The benzyl- and the xylyl nitrates were detected in the two air samples by the ion trap technology (Varian Saturn II) and were identified by reference compounds (Fig. 9).

We have used the 46 amu signal in mass selective detection as a highly specific method to analyze air samples from both the North and the South Atlantic as part of our work dealing with the global occurrence and transport of alkyl nitrates.

### 3 Pattern and levels of alkyl nitrates in air

In urban air a rather constant pattern of C3–C7 alkyl nitrates is detected by the electron capture detector (Fig. 10). As discussed before this pattern should reflect the main hydrocarbon precursors.

Alkyl nitrates as emissions from automobiles are easily detected by sampling 1–2 l of air in a public underground garage (Fig. 11) and by sampling of 4 l of air at a downtown bus stop (Fig. 12). The levels are in the range of  $5\text{--}20\text{ ng m}^{-3}$  in this case. Using a thermal desorption

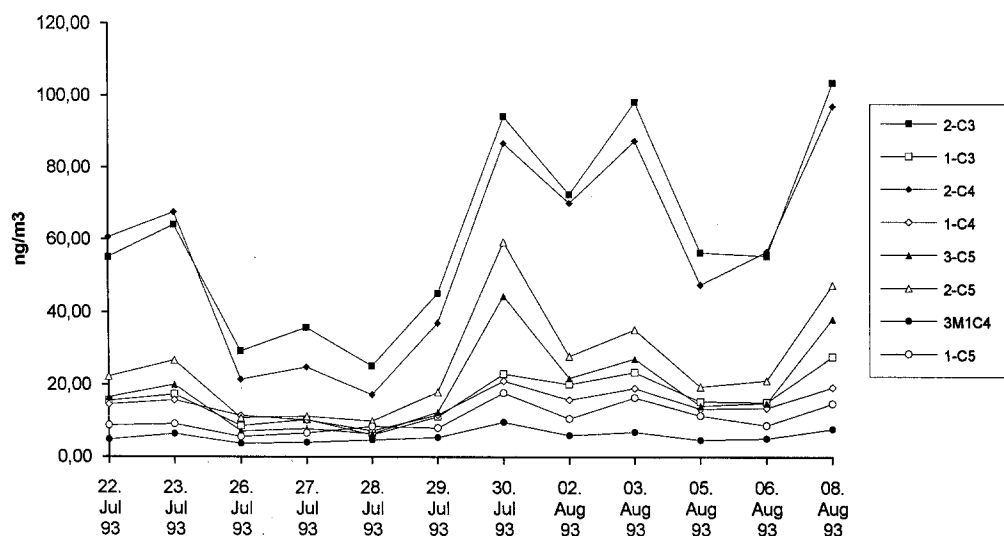


Fig. 10. Time dependence of the concentrations of various alkyl nitrates in urban air (city of Ulm) for a 16-day period

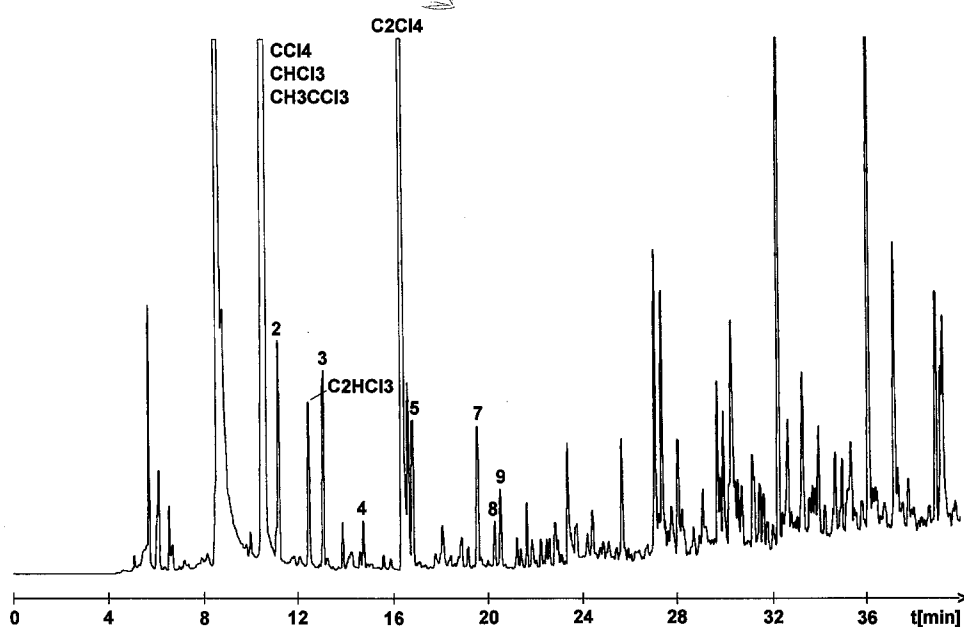


Fig. 11. HRGC (DB1701)/ECD gas chromatogram: Pattern of alkyl nitrates in 2 l air from an underground public parking garage. 2: Ethyl nitrate, 3: 2-Propyl nitrate, 4: 1-Propyl nitrate, 5: 2-Butyl nitrate + 2-Methyl-1-propyl nitrate, 6: 1-Butyl nitrate, 7: 2-Methyl-3-butyl nitrate, 8: 3-Pentyl nitrate, 9: 2-Pentyl nitrate

technique with 8–10 l of ambient air as sample volume, the pattern of the C5- and C6-alkyl nitrates in forest and alpine air could be detected by electron capture detection (ECD) and high resolution capillary gas chromatography as seen in Fig. 13 which is taken from reference [23]. Several unknown compounds could have been assigned to alkyl nitrates. Increasing the sample volume to 30–40 l using the same sampling technique records the pattern of C5- and C6-alkyl nitrates present in marine air of the North Atlantic (N 39°, W 11°) [26]. The ratio of the sampling volumes indicate the ratio of the levels of alkyl nitrates in the different types of air. Increasing the sampling volume to 100 l of marine air records a complex pattern of organic trace compounds of which only a few have been identified [24].

Levels of alkyl nitrates are mainly reported for the C1–C5 nitrates. The known preference of alkyl nitrate formation for the longer alkyl-chains [3, 6] does not ease their detection. It is compensated by a multiplicity of isomers formed, which makes a detection of the single compounds difficult. The sum of C3–C5 alkyl nitrates at a rural site in Eastern U.S. was at a level of 66 ppt(v) as compared to an about twenty times higher level of peroxy-acetyl nitrate (PAN) of 1.0 ppb(v)/5.4 ng m<sup>-3</sup> at the same site [30].

Levels of methyl nitrate were in rural northern Germany (Jülich) in the 109 ppt(v)/374.6 ng m<sup>-3</sup> range while in the Black Forest (Schauinsland) levels of 10 ppt(v)/34.4 ng m<sup>-3</sup> were measured [31]. Values of C3–C8 alkyl nitrates in continental and in marine air [32] are given in Table 4.

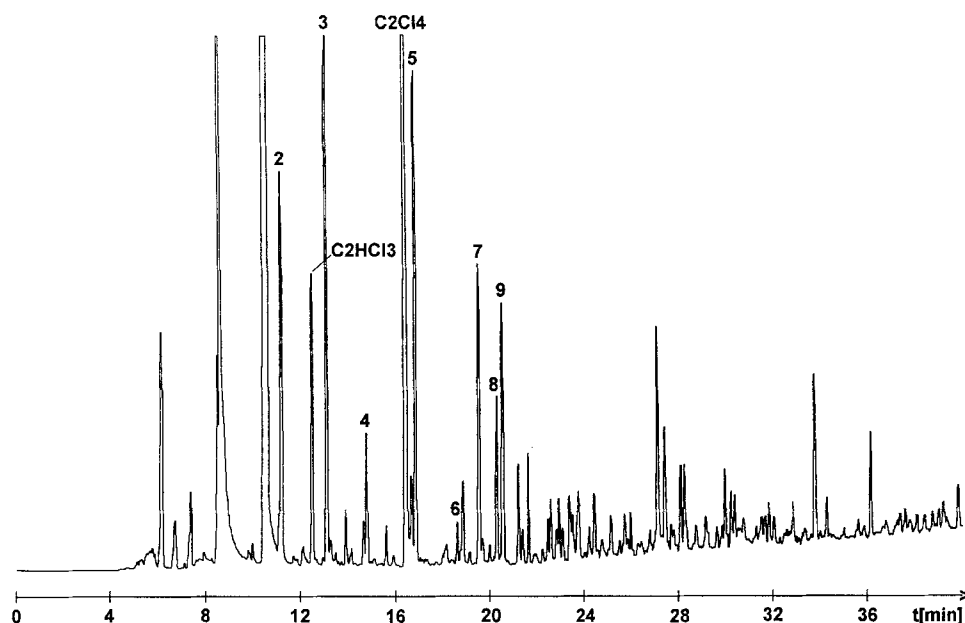


Fig. 12. HRGC (DB1701)/ECD gas chromatogram: Pattern of alkyl nitrates in 4.2 l air close to a bus station. 2: Ethyl nitrate, 3: 2-Propyl nitrate, 4: 1-Propyl nitrate, 5: 2-Butyl nitrate + 2-Methyl-1-propyl nitrate, 6: 1-Butyl nitrate, 7: 2-Methyl-3-butyl nitrate, 8: 3-Pentyl nitrate, 9: 2-Pentyl nitrate

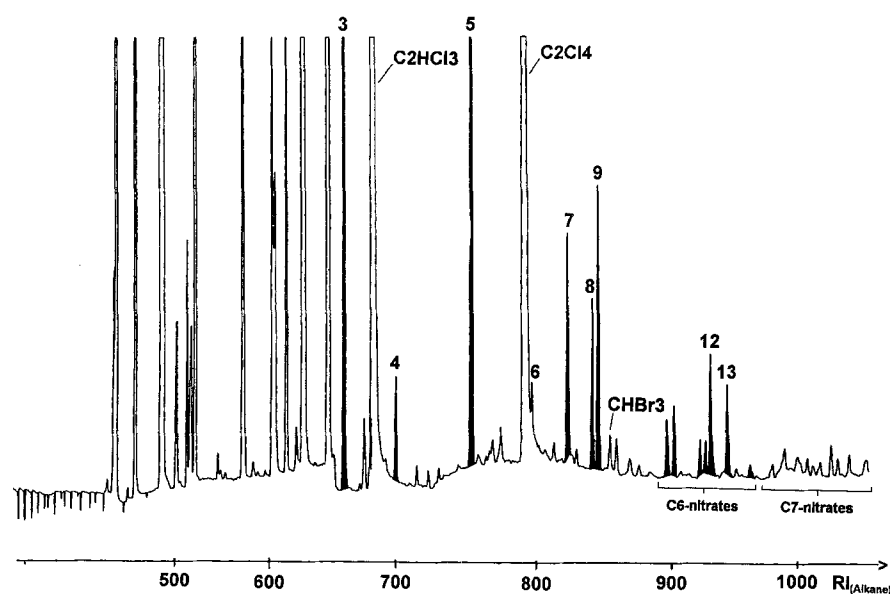


Fig. 13. HRGC (OV1)/ECD gas chromatogram: Pattern of alkyl nitrates in 4.9 l clean air (1500 m, Alps 1982) [23]. 3: 2-Propyl nitrate, 4: 1-Propyl nitrate, 5: 2-Butyl nitrate + 2-Methyl-1-propyl nitrate, 6: 1-Butyl nitrate, 7: 2-Methyl-3-butyl nitrate, 8: 3-Pentyl nitrate, 9: 2-Pentyl nitrate, 12: 3-Hexyl nitrate, 13: 2-Hexyl nitrate

#### 4 Transformation of alkyl nitrates

The long-range transport of a compound is directly connected to its stability in the air and the water environment [33].

The transformation of alkyl nitrates can occur at both moieties of the molecules, the nitric ester group and the hydrocarbon chain. Alkyl nitrates are stable enough to undergo long-range transport. The reaction rate constants of the reaction of  $\cdot\text{OH}$  radicals with alkyl nitrates are in the order of those for chloroform, trichloroethene or trichlorobenzene (Table 5).

Hydrolysis and photolytic decomposition are next to the reaction with  $\cdot\text{OH}$  radicals the major routes of abiotic transformation of alkyl nitrates in the atmosphere

particularly for the dinitrates, which are also effectively removed by wash out [34].

Hydrolysis of the nitric acid ester is a slow reaction and leads primarily to the corresponding alcohol and nitric acid. Under atmospheric conditions there will be no back reaction. Hydrolysis will be favored in water of clouds and at surfaces stabilizing the nitric acid formed, e.g. oxides or carbonates. Background levels of nitric acid in the clean marine air of the North Pacific Ocean (Mauna Loa Observatory, located 3400 m above sea level) were in the 0.02–0.03 ppb(v)/0.06–0.08  $\text{ng m}^{-3}$  range in winter increasing to 0.07–0.12 ppb(v)/0.2–0.34  $\text{ng m}^{-3}$  in summer [35]. Local events gave levels of 0.25 ppb(v)/0.7  $\text{ng m}^{-3}$  of nitric acid.



**Table 4.** C1–C8 alkyl nitrates in rural and forest air in Germany [31] and in the marine boundary layer of the Island of Hawaii [32] in ppt(v) and  $\text{ng m}^{-3}$ 

|                                     | Juelich 1988 |                 | Black Forest 1988 |                 | Hawaii 1989  |                 | Ulm 1993     |                 |
|-------------------------------------|--------------|-----------------|-------------------|-----------------|--------------|-----------------|--------------|-----------------|
|                                     | ppt(v)       | $\text{ng/m}^3$ | ppt(v)            | $\text{ng/m}^3$ | ppt(v)       | $\text{ng/m}^3$ | ppt(v)       | $\text{ng/m}^3$ |
| Methyl nitrate                      | 109          | 374.6           | 10                | 34.4            | <sup>a</sup> | –               | <sup>a</sup> | –               |
| Ethyl nitrate                       | 47.7         | 193.8           | 9.5               | 38.6            | <sup>a</sup> | –               | <sup>a</sup> | –               |
| 2-Propyl nitrate                    | 27.4         | 128.5           | 19.7              | 92.4            | 3.2          | 15              | 13.1         | 61.3            |
| 1-Propyl nitrate                    | 8.4          | 39.4            | 3.2               | 15              | 1.1          | 5.2             | 3.5          | 16.2            |
| 2-Butyl + 2-Methyl-1-propyl nitrate | 27.3         | 145.1           | 13.3              | 70.7            | 2.5          | 13.3            | 10.6         | 56.2            |
| 1-Butyl nitrate                     | <sup>a</sup> | –               | <sup>a</sup>      | –               | 0.2          | 1.1             | 2.7          | 14.4            |
| 3-Pentyl nitrate                    | <sup>a</sup> | –               | <sup>a</sup>      | –               | 0.35         | 2.1             | 3.2          | 19.3            |
| 2-Pentyl nitrate                    | <sup>a</sup> | –               | <sup>a</sup>      | –               | 0.55         | 3.3             | 4.3          | 25.8            |
| 2-Pentyl nitrate                    | <sup>a</sup> | –               | <sup>a</sup>      | –               | <sup>a</sup> | –               | 1.8          | 10.6            |
| 3-Methyl-1-butyl nitrate            | <sup>a</sup> | –               | <sup>a</sup>      | –               | <sup>a</sup> | –               | 1            | 5.8             |
| sum C5 nitrates                     | 42.0         | –               | 5.9               | –               | <sup>a</sup> | –               | <sup>a</sup> | –               |
| sum C6–C8 nitrates                  | 5.1          | –               | <2                | –               | <sup>a</sup> | –               | <sup>a</sup> | –               |

<sup>a</sup> = no value given

**Table 5.** Reaction rate constants  $K_{\text{OH}}$  ( $\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$ ) for alkyl nitrates at room temperature [43]. The  $k_{\text{OH}}$  values for methane, halomethanes and chloroethenes are given for comparison [44]. In terms of stability towards reaction with OH radicals in air the alkyl nitrates range between trichloro- and tetrachloroethene. They belong to the reactivity class 3 as defined by Ballschmiter [33]. Other compounds of this group are 1,2,4-trichlorobenzene and nitrobenzene

|                               | $K_{\text{OH}}$        | $\tau_{\text{OH}}^a$ |
|-------------------------------|------------------------|----------------------|
| Methyl nitrate                | $0.034 \cdot 10^{-12}$ | 425.5                |
| Ethyl nitrate                 | $0.49 \cdot 10^{-12}$  | 29.5                 |
| 1-Propyl nitrate              | $0.62 \cdot 10^{-12}$  | 23.3                 |
| 2-Propyl nitrate              | $0.41 \cdot 10^{-12}$  | 35.3                 |
| 1-Butyl nitrate               | $1.78 \cdot 10^{-12}$  | 8.1                  |
| 2-Butyl nitrate               | $0.92 \cdot 10^{-12}$  | 15.7                 |
| 2-Pentyl nitrate              | $1.85 \cdot 10^{-12}$  | 7.8                  |
| 3-Pentyl nitrate              | $1.12 \cdot 10^{-12}$  | 12.9                 |
| 2-Hexyl nitrate               | $3.17 \cdot 10^{-12}$  | 4.6                  |
| 3-Hexyl nitrate               | $2.70 \cdot 10^{-12}$  | 5.4                  |
| 3-Heptyl nitrate              | $3.69 \cdot 10^{-12}$  | 3.9                  |
| 3-Octyl nitrate               | $3.88 \cdot 10^{-12}$  | 3.7                  |
| $\text{CH}_4$                 | $0.83 \cdot 10^{-14}$  | 1743                 |
| $\text{CH}_3\text{Cl}$        | $4.4 \cdot 10^{-14}$   | 329                  |
| $\text{CH}_3\text{Br}$        | $3.9 \cdot 10^{-14}$   | 371                  |
| $\text{CH}_2\text{Cl}_2$      | $0.14 \cdot 10^{-12}$  | 103                  |
| $\text{CHCl}_3$               | $0.1 \cdot 10^{-12}$   | 145                  |
| $\text{CCl}_4$                | $< 4 \cdot 10^{-16}$   | –                    |
| $\text{CHCl} = \text{CCl}_2$  | $2.2 \cdot 10^{-12}$   | 7                    |
| $\text{CCl}_2 = \text{CCl}_2$ | $0.17 \cdot 10^{-12}$  | 85                   |

<sup>a</sup>  $\tau_{\text{OH}}$ : lifetime (in days), defined by  $c_0 \rightarrow c_0/e$ .  $\tau_{\text{OH}} = 1/(K_{\text{OH}} \cdot c_{\text{OH}})$ . Calculated for an average concentration of OH radicals of  $0.8 \cdot 10^6$  (molecules  $\text{cm}^{-3}$ ) in air

Faster than the hydrolysis by alkaline hydroxides that is quite slow is the reaction with  $\text{NH}_4\text{OH}$  [36]. Degradation by  $\text{NH}_4\text{OH}$  can be used to eliminate nitrates in a sample solution and thus give a first indication of their presence.

Aldehydes can be directly formed in a second type of alkyl nitrate hydrolysis under alkaline and neutral conditions undergoing alpha-hydrogen elimination. This reac-

tion leads to the nitrite ion and the corresponding aldehyde. While methyl nitrate only forms traces of formaldehyde by this way, the benzyl nitrate results in a 90% formation of benzaldehyde by this reaction [18]. Benzaldehyde is a major compound in organic flame chemistry. One might speculate whether in its formation in flame chemistry the benzyl nitrate acts as a general precursor. 2-Methyl benzaldehyde, dimethyl benzaldehydes, and trimethyl benzaldehydes have been identified as emissions from non-catalyst and catalyst automobiles and from heavy-duty diesel trucks as well [37]. The corresponding nitrates have been identified in the air of a parking lot (Fig. 11).

As a third transformation type elimination of a beta-hydrogen is possible, leading to an olefine and the nitrate ion. This reaction is strongly dependent on the structure of the alkyl nitrate. It is a major pathway for the decomposition of branched nitrates like the tert-butyl nitrate (2,2-dimethyl-ethyl nitrate). [38]

Reactions initiated by an \*OH radical at the alkyl-chain of alkyl nitrates would finally lead to alkyl dinitrates and/or to keto- and aldo-alkyl nitrates, respectively. Table 5 summarizes the reaction rate constants of alkyl nitrates with \*OH radicals. The rate constants are in the same range for ethyl nitrate to octyl nitrate. The  $k_{\text{OH}}$  reaction rate constants of propane to octane are similar to those of the alkyl nitrates.

Recently methyl tert-butyl ether and ethyl tert-butyl ether are becoming of increasing importance as high-octane fuel additives. The air chemistry of this compounds may also lead to organic nitrates [39].

Photolysis of alkyl nitrates (< 330 nm) leads to  $\text{NO}_2$  and an alkoxy radical  $\text{RO}^*$  which will continue the known air chemistry of this type of radicals which has already been discussed in the beginning of the paper and in the reaction scheme 1 [40, 41]

For the discussion of the ECD signals observed in marine air [24], which are not explained by halogenated

compounds the following groups of difunctional nitrates among others have to be considered:

- (1)  $O_2NOH_2C-(CH_2)_x-CH_2ONO_2$   
(alkyl-dinitrates, dinitroxy-alkanes)
- (2)  $R-CH(OH)-(CH_2)_x-CH_2ONO_2$   
(hydroxy-nitrates, nitroxy-alcohols)
- (3)  $R-CH(ONO_2)OCH_2-R$   
(ether-nitrates, nitroxy-ether)
- (4)  $H-C(O)-(CH_2)_x-CH_2ONO_2$   
(aldo-nitrates, nitroxy-aldehydes)
- (5)  $R-C(O)-(CH_2)_x-CH_2ONO_2$   
(keto-nitrates, nitroxy-ketones)
- (6)  $HOOC-(CH_2)_x-CH_2ONO_2$   
(carboxy-nitrates, nitroxy-carboxylic acids)

Systematically these compounds are also considered as "nitro-oxy", mostly written as "nitroxy", substituted parent compounds. They can be formed starting with the alkyl nitrate or vice versa with the corresponding parent molecule, e.g. the ether, aldehyde or ketone. These difunctional compounds have been observed in chamber experimental studies and might also be found adsorbed on atmospheric particles [42]. The microchemical techniques for synthesizing nitrate ester derivatives described in the foregoing will allow to elucidate most of the unknowns observed by the ECD in air. This work is in progress. The synthesis and analytical chemistry of hydroxy-nitrates (nitroxy alcohols) has recently been described [27].

## 5 Conclusions

Alkyl nitrates form a broad spectrum of natural and anthropogenic organic trace compounds in air which so far has only given in part the necessary attention. The basic air chemistry of these compounds has been known for long. The analytical tools for sampling, separation and detection of traces of alkyl nitrates with carbon numbers more than 5 can be easily optimized on the basis of general analytical principles. Reference standards either as single compounds or as mixtures of increasing complexity can be obtained by various micropreparation methods. The reaction of alkanes with nitric acid has the potential of simulating the alkyl nitrate formation in air. The environmental impact of the occurrence of different groups of alkyl nitrates has to be evaluated yet. Their function as precursors of  $HNO_3$  and nitrate depositions and the basic physiological potential at least their vasodilative effects to men are known.

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**Note added in proof**

Alkyl nitrates up to pentadecyl nitrate have been identified in urban and rural air. They form a complex pattern of isomers with the dominant being the  $(n + 1)$  nitrate of the respective n-alkanes [Luxenhofer O, Ballschmiter K (1994) *Fresenius J Anal Chem* 350:395–402