absorption correction based on azimuthal scans was applied. The structure was solved by direct methods (SHELXS-86) followed by Fourier cycles, $R = 0.036$, $R_w = 0.027$ for 712 variable parameters, GOF = 1.73. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101766. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Organic Nitrates of Isoprene as Atmospheric Trace Compounds**

Gerhard Werner, Jürgen Kastler, Ralf Looser, and Karlheinz Ballschmiter*

Isoprene (2-methyl-1,3-butadiene) is a terpene building block which is emitted preferentially by oaks, but also by other plants, as well as algae.[1] As such, it was examined early on with respect to its broad reaction potential as a butadiene derivative in connection with natural smog formation in the atmosphere.[2] It is by far the single compound biologically emitted in the largest amounts. On a global average, the annual emission of isoprene is an estimated 450 Tg (1 Tg = 1×10^6 tons).[3] After the addition of an OH radical to an isoprene double bond, follow-up reactions with oxygen in the atmosphere lead to the formation of methacrolein ($H_2C{=}C(CH_3)CHO$) and methyl vinyl ketone ($H_2C{=}CHCOCH_3$).[4] Both are also formed in the reaction of isoprene with ozone[5] and were detected in the ambient air; their concentration in the atmosphere shows strong seasonal fluctuations with a maximum in the summer.[4, 6]

According to smog chamber experiments, further products of the reaction of isoprene in the $OH/O_2/NO$ system are 3-methylfuran, hydroxymethyl vinyl ketone, C5-carbonyl compounds, and unspecified organic nitrates.[7] 3-Methylfuran could be detected in forest air.[8] The identification of a peroxyacetyl nitrate analogue of isoprene was the entry of the chemistry of isoprene into the group of "odd nitrogen compounds" (NO_y).[9] Smog chamber experiments on the reaction of isoprene with NO_3 radicals in the dark, simulating night chemistry, led to the known products methacrolein, methyl vinyl ketone, and C5-hydroxycarbonyl compounds as well as C5-aldonitrates such as $O_2NOCH_2C(CH_3){=}CHCHO$ (**13**, **14**), C5-hydroxynitrates such as $O_2NOCH_2C(CH_3){=}CHCH_2OH$ (**5**, **6**), and C5-hydroperoxynitrates such as $O_2NOCH_2C(CH_3){=}CHCH_2OOH$, as shown by atmospheric pressure ionization tandem mass spectrometry (API-MS/MS).[10, 11] This range of products indicates the possibilities of the night chemistry of isoprene in NO_2- and ozone-rich air, in which NO_3 radicals are formed. Such an atmospheric situation usually builds up from traffic emissions when there is a high amount of sunshine during the day (areas of high pressure in temperate zones such as Europe; normal weather conditions in California).

If one considers the reactions that a compound can in principle undergo in the atmosphere, and if the corresponding

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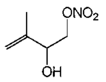
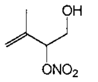
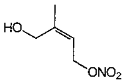
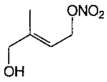
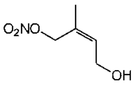
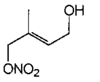
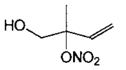
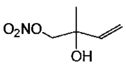
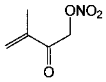
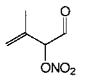
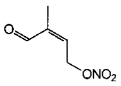
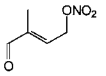
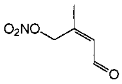
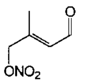
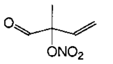
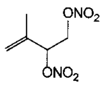
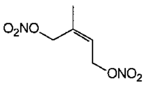
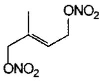
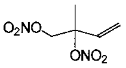
possible reaction products are available as reference substances, the analytical parameters of the compound can be examined and optimized substance specifically for effective enrichment, separation and detection. This strategy allowed us to detect long-chain alkyl nitrates and a broad spectrum of dinitrates and hydroxynitrates of short-chain hydrocarbons in continental and marine air down to the lower ng m^{-3} range for the first time.[12] Table 1 summarizes the possible isomers of the dinitrates, hydroxynitrates, and aldo/ketonitrates of isoprene retaining one of the double bonds. We obtained the following compounds in microsyntheses: **2**–**7**, **11**–**14**, **16**–**18**. The corresponding synthetic routes, starting out from epoxides and bromo and hydroxy derivatives of isoprene, are based on the respective literature procedures.[13] Because of the variety of possible mono- and multifunctional organonitrates, Schneider and Ballschmiter[14] developed a systematic nomenclature in short style based on the parent hydrocarbon which deviates from the IUPAC nomenclature. This is to be found in the penultimate column of Table 1. It is also used in the captions of the chromatograms in Figure 1.

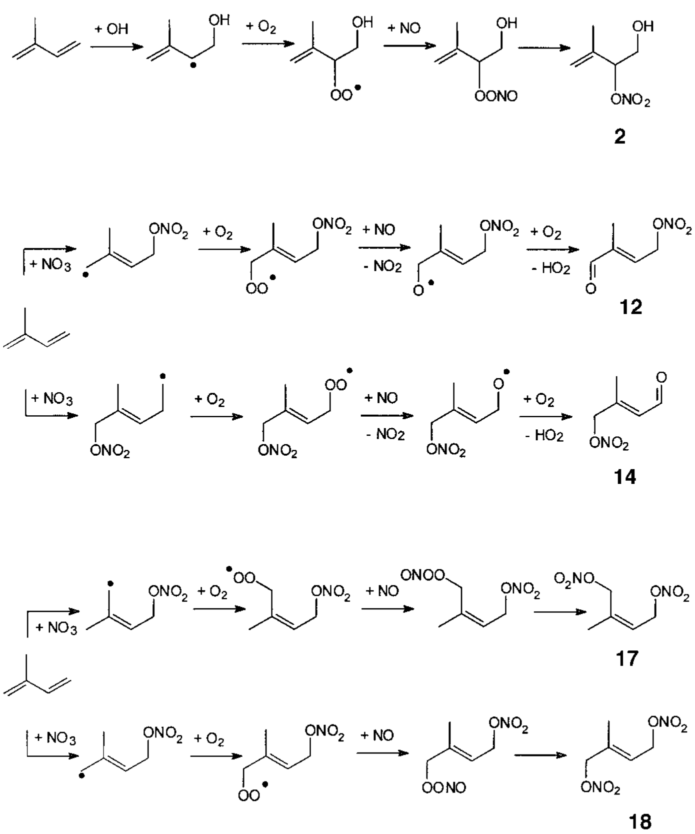
We report on the structure-specific synthesis of organic nitrates of isoprene, on the stability of these compounds under the conditions of a high-volume adsorptive sample collection on silica gel, and on a determination in the ng m^{-3} range by means of high-resolution gas chromatography/negative chemical ionization-mass spectrometry (HRGC/NCI-MS), which is preceded by a group-selective preseparation by means of normal-phase HPLC.[15] With this method, the following five organic nitrates of isoprene retaining one of the double bonds were detected in ambient air for the first time: *cis*- and *trans*-2-methyl-2-butene-1,4-dinitrate (**17** and **18**, respectively), 3-methyl-2-nitrooxy-3-butene-1-ol (**2**), *trans*-2-methyl-4-nitrooxy-2-butenal (**12**), and *trans*-3-methyl-4-nitrooxy-2-butenal (**14**).[16] According to a first quantitative estimate, the concentrations of the identified compounds lie in the lower ppt(v) range at a few ng m^{-3}. Thus, besides the two dinitrates **17** and **18**, the C5-hydroxynitrates ($H_2C{=}C(CH_3)CH(ONO_2)CH_2OH$) and C5-aldonitrates ($O_2NOCH_2CH{=}C(CH_3)CHO$ and $O_2NOCH_2C(CH_3){=}CHCHO$) of isoprene,[10, 11] so far described only in chamber experiments, have now also been detected in the ambient air for the first time with compounds **2**, **12**, and **14**.

The method of formation of the described organic nitrates of isoprene can be formulated as shown in Scheme 1. The proposed mechanisms for isoprene[11, 17] as well as those already

Table 1. Hydroxynitrates, aldo/ketonitrates, and dinitrates of isoprene which can be formed unter retention of one of the double bonds.[a]

Entry	IUPAC nomenclature	Our nomenclature	Structure
1	3-methyl-1-nitrooxy-3-buten-2-ol **1**	2M1en3OH4C4	
2	3-methyl-2-nitrooxy-3-buten-1-ol **2**	2M1en4OH3C4	
3	*cis*-2-methyl-4-nitrooxy-2-buten-1-ol **3**	c-2M2en1OH4C4	
4	*trans*-2-methyl-4-nitrooxy-2-buten-1-ol **4**	t-2M2en1OH4C4	
5	*cis*-3-methyl-4-nitrooxy-2-buten-1-ol **5**	c-2M2en4OH1C4	
6	*trans*-3-methyl-4-nitrooxy-2-buten-1-ol **6**	t-2M2en4OH1C4	
7	2-methyl-2-nitrooxy-3-buten-1-ol **7**	2M3en1OH2C4	
8	2-methyl-1-nitrooxy-3-buten-2-ol **8**	2M3en2OH1C4	
9	3-methyl-1-nitrooxy-3-buten-2-on **9**	2M1en3O4C4	
10	3-methyl-2-nitrooxy-3-butenal **10**	2M1en4O3C4	
11	*cis*-2-methyl-4-nitrooxy-2-butenal **11**	c-2M2en1O4C4	
12	*trans*-2-methyl-4-nitrooxy-2-butenal **12**	t-2M2en1O4C4	
13	*cis*-3-methyl-4-nitrooxy-2-butenal **13**	c-2M2en4O1C4	
14	*trans*-3-methyl-4-nitrooxy-2-butenal **14**	t-2M2en4O1C4	
15	2-methyl-2-nitrooxy-3-butenal **15**	2M3en1O2C4	
16	3-methyl-3-butene-1,2-dinitrate **16**	2M1en3,4C4	
17	*cis*-2-methyl-2-butene-1,4-dinitrate **17**	c-2M2en1,4C4	
18	*trans*-2-methyl-2-butene-1,4-dinitrate **18**	t-2M2en1,4C4	
19	2-methyl-3-butene-1,2-dinitrate **19**	2M3en1,2C4	

[a] Compounds **2**–**7**, **11**–**14**, and **16**–**18** were synthesized in the course of this work.



Scheme 1. Atmospheric decomposition of isoprene in NO_x-containing air, initiated by OH or NO_3 radicals, leading to the formation of hydroxynitrates, dinitrates, and aldo/ketonitrates.

proved for aliphatic hydrocarbons are shown.[18] The subsequent behavior of these compounds is characterized by an addition of OH or NO_3 radicals to the double bond with the corresponding follow-up reactions. In the daytime, photolytic decay is also possible. As NO_2 and the corresponding alkoxy radical are generated in the course of this decay, the formation of the direct precursors of **12** and **14** by degradation of **18** is feasible. However, it has been shown that for unsaturated nitrates photolysis is of lesser importance than degradation by OH radicals.[19]

The investigations into the optimization of the analytical procedure showed that **12** slowly decomposes on silica gel, even when the sample is cooled. Likewise, the reference compounds *cis*- and *trans*-2-methyl-4-nitrooxy-2-buten-1-ol (**3** and **4**, respectively) are not sufficiently stable for the described workup. Their occurrence in ambient air can therefore neither be proved nor excluded at present. We are working on an optimization of the method for these compounds and at the same time attempting to increase the frequency of sample collection. The air samples we checked so far for the presence of organonitrate derivatives of isoprene were all collected on the campus of the University of Ulm, which is located at an elevation of 610 m above sea level at the southern decline of the Swabian Mountains above the city of Ulm in a wooded area mainly populated by oak trees. Around the university buildings a large area is designated as parking space. The air samples were collected in this area.

The conditions of the high-volume sample collection (50–100 m^3) on ultrapure silica gel have already been described in detail.[20] The desorption of the polar organic nitrates was done with 300 mL of pentane/acetone (4:1 w/w). The workup of the extracts by means of an NP-HPLC group separation with a nitrate phase[15] already results in an extensive separation according to the functional groups present. The subsequent separation of the LC fractions by high-resolution capillary gas chromatography with mass-selective detection of the respective isoprene nitrates by indicator fragments (Table 2) after negative chemical ionization mass spectrometry (NCI-MS) takes up previously described analytical procedures.[15] The retention behavior of the target compounds was determined with the corresponding reference substances by means of high-resolution capillary gas chromatography. Identical retention times on two phases of different polarity and the respective substance-specific NCI-MS signal were rated as positive proof of the occurrence in the sample of ambient air. The result of the analysis of a sample of 50 m^3 of air that was collected on May 28, 1998 between 3:00am and 7:00am on the university campus is shown as an example in Figure 1. Six HRGC/(methane)-NCI-MS chromatograms of the NP-HPLC fraction containing the aldo/ketonitrates as well as the hydroxynitrates are shown.[16] The identification of the dinitrates was carried out in analogy. The individual capillary gas chromatograms were generated by detection at different mass traces which are characteristic for the molecules (selected ion monitoring, SIM). Only by means of this selective mass spectrometric detection which eliminates the influence of interfering components did the identification of organonitrate derivatives of isoprene in the atmosphere become possible, to our knowledge for the first time. It is our aim to quantify the identified compounds and to become able to analyze the so far elusive isoprene nitrates in air samples by modifying the described procedure.

Table 2. The respective six highest (methane) NCI-MS signals (*m*/*z*) of five isoprene nitrates identified in air samples.[a]

Entry	Isoprene nitrate	*m*/*z* [amu] (rel. signal height [%])
1	**2**	101 (100), 46 (30), 99 (9), 77 (7), 102 (6), 71 (4)
2	**12**	98 (100), 62 (88), 99 (42), 46 (12), 69 (7), 97 (6)
3	**14**	62 (100), 98 (77), 99 (43), 46 (13), 69 (7), 97 (6)
4	**17**	62 (100), 46 (18), 98 (5), 99 (4), 101 (2), 97(1)
5	**18**	62 (100), 46 (22), 98 (7), 99 (7), 81(2), 71(2)

[a] The values in parentheses state the relative heights of the signal as a percentage relative to the height of the most intense signal.

Experimental Section

Figure 1 shows gas chromatograms of an air sample which were obtained with an MN-Optima-1701 capillary column (Macherey-Nagel, Düren, Germany; length 50 m, inner diameter 0.32 mm, film thickness 0.21 µm, carrier gas helium 4.6). After the on-column injection on an HP-5890 gas chromatograph (Hewlett Packard, Palo Alto, USA), the separation took place in the temperature-programmed mode (40 °C (5 min), 3 °C min^{-1}, 160 °C (30 min)). NCI-MS in the selected-ion mode (reactant gas methane, $10^{-3.8}$ mbar) on a VG Micromass TS 250 mass spectrometer (VG Tritech,

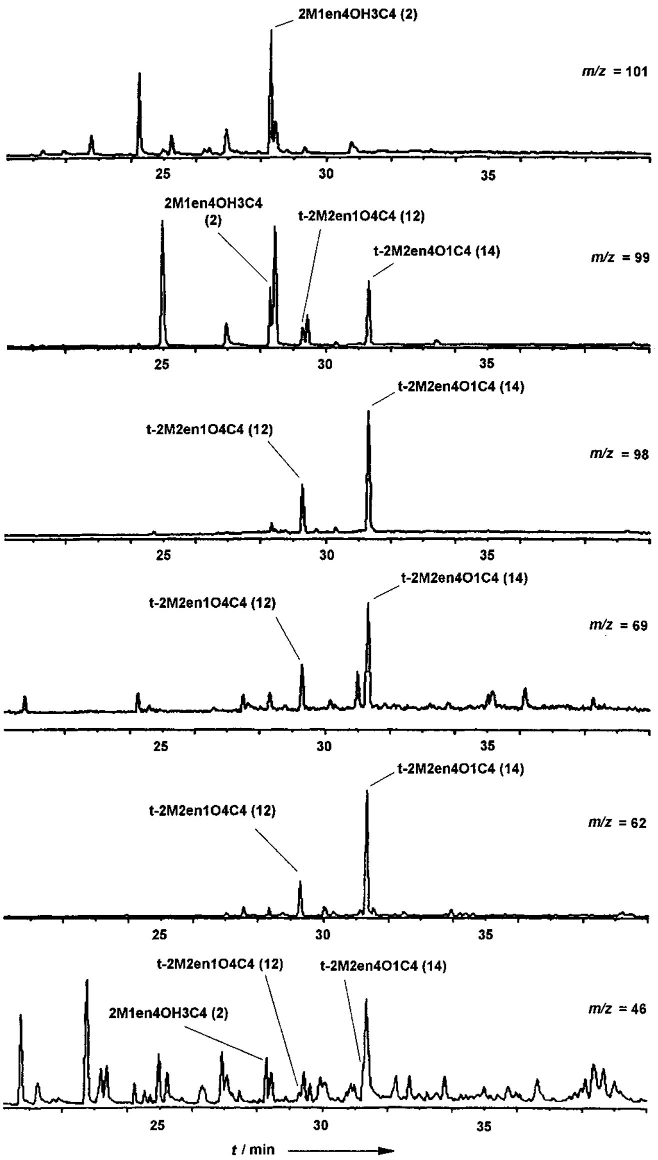


Figure 1. HRGC/(methane)-NCI-MS chromatograms of an air sample (hydroxy- and aldo/ketonitrate fractions, respectively, of the HPLC group separation), recorded in the SIM mode for six different *m*/*z* ratios. Two aldonitrates (**12**, **14**) and one hydroxynitrate (**2**) were identified.

Manchester, Great Britain) was used for detection (ionization energy 50 eV, source temperature 100 °C).

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