Final-term report (01.03.2012 – 31.08.2013)

BELGIAN FEDERAL SCIENCE POLICY – RESEARCH FELLOWSHIP (to NON-EU POSTDOCS)
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Introduction

The performed research relates to on-going activities of the host unit within the frame of the project "Biogenic Influences on Oxidants and Secondary Organic Aerosol: theoretical, laboratory and modeling investigations (BIOSOA)"; more specifically, it concerns the following two task:

Task 3.1 Chemical formation pathways leading to isoprene secondary organic aerosol (SOA) tracers;

and

Task 3.4 Development of analytical methodology based on liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) for quantifying the contributions of individual biogenic volatile organic compounds to the organic aerosol.

Background and Objectives

Isoprene is the largest source of nonmethane hydrocarbons in the atmosphere, estimated at about 500 Tg C/year (Guenther et al., 1995). It is mainly emitted by broadleaf vegetation and plays a critical role in tropospheric chemistry over large regions of the globe. In pristine regions such as the Amazon rainforest, the oxidation of isoprene by the hydroxyl (OH) radical occurs in the presence of low NO_x ($NO + NO_2$) concentrations, whereas in polluted regions the photooxidation occurs in the presence of high NO_x concentrations. The underlying chemistries leading to particle-phase products, however, are not fully understood. Major marker compounds of secondary organic aerosol (SOA) from isoprene photooxidation are the diastereoisomeric 2-methyltetrols (2-methylthreitol and 2-methylerythritol), the isomeric C_5-alkene triols [2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene], and 2-methylglyceric acid. The 2-methyltetrols and the C_5-alkene triols were first discovered in fine aerosol collected from the Amazon forest (Claeys et al., 2004a; Wang et al., 2005), whereas 2-methylglyceric acid was first detected in fine aerosol collected from K-puszta, Hungary (Claeys et al., 2004b). Laboratory experiments demonstrated that these SOA marker compounds can be formed through photooxidation of isoprene under different conditions; while the 2-methyltetrols are formed under various NO_x regimes (Edney et al., 2005; Surratt et al, 2006), the formation of the C_5-alkene triols requires low-NO_x conditions in contrast to that of 2-methylglyceric acid which is enhanced under high-NO_x conditions (Surratt et al, 2006).

Isoprene SOA chemistry is tightly linked to gas-phase photooxidation processes, which yield a number of volatile gas-phase products, including methacrolein, methyl vinyl ketone, methyl furan,

C_5-alkene diols and C_5-hydroxyhydroperoxides as first-generation products (Miyoshi et al., 1994; Ruppert and Becker, 2000; Kleindienst et al., 2009; Paulot et al., 2009; Surratt et al., 2010). Different mechanistic pathways, involving gas- and particle-phase reactions, have been suggested to explain the formation of the 2-methyltetrols through photooxidation of isoprene under low NO_x conditions in the presence or absence of acidic or neutral ammonium sulfate seed aerosol (Claeys et al., 2004a; Claeys et al., 2004b; Böge et al., 2006; Kleindienst et al., 2009; Paulot et al., 2009; Surratt et al., 2010). Key intermediates in the pathway first reported by Claeys et al. (Claeys et al., 2004a) and later elaborated by Böge et al. (Böge et al., 2006) and Kleindienst et al. (Kleindienst et al., 2009) are the C_5-alkene diols, whereas those in the pathway reported by Paulot et al. (Paulot et al., 2009) are the C_5-epoxydiols. With regard to the first pathway, it has been shown by Böge et al. (Böge et al., 2006) that the C_5-alkene diol, 1,2-dihydroxy-2-methyl-3-butene, serves as a precursor for the 2-methyltetrols. In the present work, we have further evaluated whether isomeric C_5-alkene diols, which have first been detected upon photooxidation of isoprene in the absence of NO and are known to be formed in the ambient atmosphere (Kleindienst et al., 2009), can serve as precursors for the 2-methyltetrols, C_5-alkene triols, and 2-methylglyceric acid under low-NO_x conditions.

Experimental Section

***Preparation and characterisation of C_5-alkene diols**:* Three different positional isomers of the C_5-alkene diols were synthesized according to published procedures. 1,2-Dihydroxy-2-methyl-3-butene (diol 1) (**1**) was prepared by hydrolysis of 2-methyl-2-vinyloxiran (Ruppert and Becker, 2000). 1,2-Dihydroxy-3-methyl-3-butene (diol 2) (**2**) was prepared from 3,4-epoxytetrahydrofuran in an alkylative double ring opening reaction with methyl lithium (Hodgson et al., 2001). 1,4-Dihydroxy-2-methyl-2-butene (diol 3) (**6**) was obtained in a 3-step reaction starting from isoprene, involving bromination of isoprene, replacement of the bromine groups by acetate groups, and saponification (Ruppert and Becker, 2000). The synthesized C_5-alkene diols were characterized by ^{1}H-NMR and EI-MS of their TMS derivatives.

***Smog chamber experiments**:* Chamber experiments were conducted at the Leibniz-Institut für Troposphärenforschung (TROPOS), using the LEAK chamber (volume: 19 m^3), which was described by Iinuma et al. (Iinuma et al., 2009). The experiments were mainly photooxidation experiments under dry conditions using H_2O_2 as oxidant, except for one ozonolysis experiment at a RH 30%, and were carried out in the absence of NO_x and using neutral see particles. In total, 12 chamber experiments were performed: 4 with isoprene, 2 with diol 1, 4 with diol 2, and 2 with diol 3. The initial hydrocarbon concentration was about 100 ppb. The SOA samples were collected on a Teflon filter (47-mm diameter, Pallflex T60A20, Pall, NY, USA) after the reaction was terminated by switching off the UV-lamps. The sampling time was 1 h with a total sampling volume of 1.8 m^3, except in the time-resolved experiments, where the sampling time was 10 min. For the final SOA collections, XAD-4 coated denuders (5 channel, 400 mm length, URG, Chapel Hill, NC, USA) were installed in front of the filter pack to remove semi-volatile compounds. The filter samples were stored in a freezer (-20 °C) until analysis. In selected experiments with isoprene 500 mL of the gas phase was bubbled through a solution of acidified methanol (20 mL; 1% HCOOH) kept in a glass bottle at 0 °C in an effort to trap C_5-epoxydiols and convert them to the 2-methyltetrol mono-methylethers through acid-catalyzed opening of the oxiran ring and reaction with methanol.

***GC/MS analysis**:* All filters were analyzed for polar compounds by GC/MS with prior trimethylsilylation using a method that was adapted from that reported by Pashynska et al. (Pashynska et al., 2002). The identity of the compounds was confirmed by comparing the EI mass spectral data with those reported in the literatures (Claeys et al., 2004a; Claeys et al., 2004b; Wang et al., 2005).

***LC/MS analysis**:* LC/MS measurements were performed using the same LC system described in the previous work (Shalamzari et al., 2013). A C_{18} Gold column was employed and ion-pairing (IP) reagent dibutylammonium acetate (DBAA) was used in mobile phase. The isoprene SOA-related organosulfates (OSs) in the ambient sample were assigned based on comparison of their $[M - H]^-$ MS^2 product ion spectra with those previously reported (Gómez-González et al., 2008; Safi Shalamzari et al., 2013). A mixture of four commercially available compounds including three organosulfonates as surrogate compounds for organosulfates, i.e., methane sulfonate (MSA), ethane sulfonate (ES), 2-propyl sulfonate (PS), and D-galactose 6-sulfate (GS), was employed to develop the ion-pairing LC/MS method for the analysis of small polar organosulfates.

***Aerosol sampling**:* Archived PM2.5 (particulate matter with an aerodynamic diameter ≤ 2.5 um) aerosol samples collected on quartz fibre filters were analyzed in the same way as SOA samples. The ambient aerosol samples were collected during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for BIOgenic atmospheric aeroSOLs) campaign, which took place from 24 May to 29 June 2006 at K-puszta, Hungary, a rural site located on the Great Hungarian Plain (46°58’N, 19°35’E, 125 m above sea level), 15 km northwest from the nearest town Kecskemét, and 80 km southeast from Budapest. For more information on this campaign, and collection and storage of the samples, see Maenhaut et al. (Maenhaut et al., 2008).

Results and Discussion

Chemical formation pathways study: GC/MS results

Figure 1 shows extracted ion chromatograms (EICs) (*m/z* 219 + 231) obtained for ambient PM2.5 aerosol collected from K-puszta, Hungary, and selected SOA samples from the chamber (without added NO) in the presence of neutral ammonium sulfate seed aerosol. The 2-methyltetrols (i.e., 2-methylthreitol and 2-methylerythritol) are detected as abundant marker compounds in the photooxidation of isoprene and the isomeric C_5-alkene diols, whereas the C_5-alkene triols are only detected in ambient PM2.5 aerosol and in the SOA samples from the chamber irradiation of isoprene with ozone or H_2O_2. It thus appears that under the chamber conditions the C_5-alkene diols serve as gas-phase intermediates for the 2-methyltetrols but not for the C_5-alkene triols.

Table 1 shows the concentrations of SOA tracers formed from the irradiation reactions and their percentage contributions to the sum of all tracers; the last two columns of Table 1 give the concentration of the total SOA mass and the percentage contribution of the sum of all tracers to the total SOA mass. It can be seen in Table 1 that in the case of the time-resolved SOA collections for the diol 2 and 3 experiments (experiments 10 and 12) the percentage contribution of the sum of all tracers to the total SOA mass is the highest for the first collection (after 10 min), indicating a fast formation of the major tracers, i.e., the 2-methyltetrols, which together account for over 80% of the sum of all tracers, and thus suggesting that the 2-methyltetrols are not stable in the course of the experiment. Table 2 lists the average percentage contributions to the sum of all tracers and average *threo/erythro* ratios per type of experiment; the average for the diol 2 experiments were calculated with the data from the final aerosol collection (i.e., experiments 7 and 9). It is worth noting in Table 2 that the *threo*/*erythro* ratio of the 2-methyltetrol diastereoisomers is different for the isoprene and C_5-alkene diol experiments, with the highest ratio for diol 1 (0.72; Fig. 1D) and the lowest ones for diols 2 and 3 (0.35; Figs. 1E and 1F), indicating that diol 1 favors the formation of 2-methylthreitol, whereas diols 2 and 3 favor that of 2-methylerythritol. Interestingly, the overall average

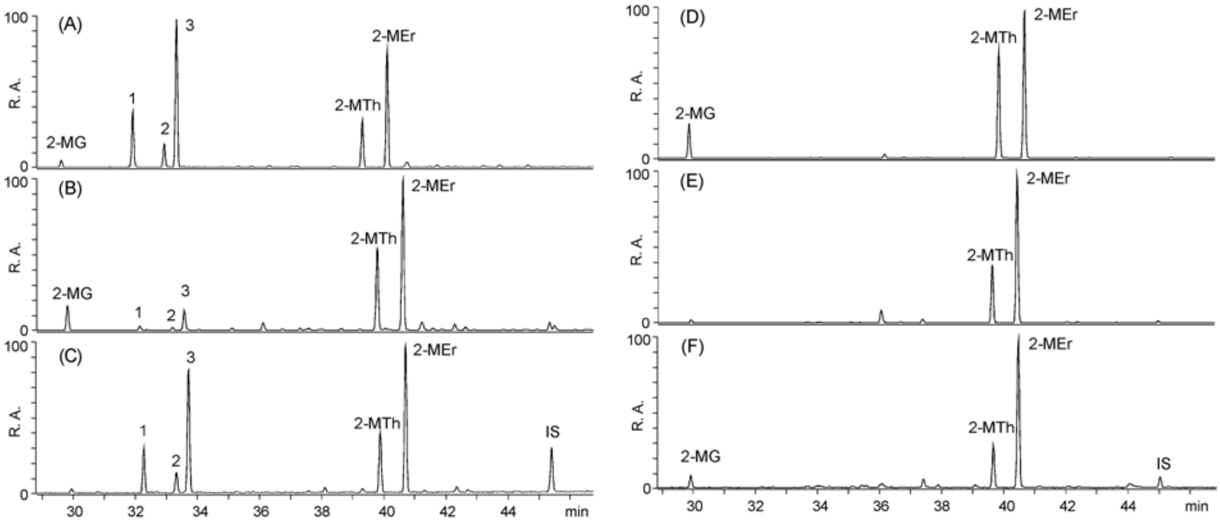


Figure 1. GC/MS extracted ion chromatograms (*m/z* 219 + 231) obtained for SOA from ambient aerosol sample collected in K-puszta, Hungary (A), the photooxidation of isoprene with OH, expt. 1 (B), isoprene with ozone, exp. 2 (C), and 1,2-dihydroxy-2-methyl-2-butene, exp. 5 (D), 1,2-dihydroxy-3-methyl-3-butene, exp. 9 (E), and 1,4-dihydroxy-2-methyl-2-butene (*cis* + *trans*), exp. 11 (F) with OH. Abbreviation: 2-MG: 2-methylglyceric acid; **1**: *cis*-2-methyl-1,3,4-trihydroxy-1-butene; **2**: 3-methyl-2,3,4-trihydroxy-1-butene; **3**: *trans*-2-methyl-1,3,4-trihydroxy-1-butene; 2-MTh: 2-methylthreitol; 2-MEr: 2-methylerythritol; R.A., relative abundance; IS: internal standard.

threo/*erythro* ratio of the 2-methyltetrols for the three isomeric C_5-alkene diols (0.48) falls between those obtained in the isoprene/O_3 experiment (0.42) and the photooxidation of isoprene (0.57). Table 2 further shows that the percentage contributions of the 2-methyltetrols to the sum of all tracers were above 50% for the isoprene experiments (i.e., 67% for isoprene/OH and 51% for isoprene/O_3) and were even higher for the C_5-alkene diol experiments (i.e., 81% for diol 1, 93% for diol 2, and 85% for diol 3).

Furthermore, it can be seen that 2-methylglyceric acid is not only formed from isoprene but also from certain C_5-alkene diols (Fig. 1); the percentage of the mass fraction of 2-methylglyceric acid to the sum of all tracers amounts to 11%, 16% and 13% for the isoprene/OH, the diol 1/OH, and the diol 3/OH reactions, respectively (Table 2). Relatively less 2-methylglyceric acid is formed in the diol 2/OH reaction (4%) and little upon isoprene ozonolysis (0.7%).

The question arises whether the applied chamber conditions reflect those encountered under ambient conditions, as will be discussed in this and the following paragraphs. Kleindienst et al. (Kleindienst et al., 2009) proposed a gas-phase mechanism for the formation of the 2-methyltetrols from isoprene through C_5-alkene diols and peroxide radicals involving trihydroxyperoxy radicals which might react with HO_2 to form C_5-trihydroxyhydroperoxides and partition to the particle phase [Scheme 1(A)]. In the present study, however, no evidence could be found for the formation of C_5-trihydroxyhydroperoxides; if such hydroperoxide products would have been formed and would be stable under our conditions, we would expect the formation of oxo derivatives as thermal degradation products of the trimethylsilylated hydroperoxides upon GC/MS analysis, similar to the behavior of trimethylsilylated unsaturated fatty acid hydroperoxides (Grechkin et al., 2005). The photooxidation experiments with isoprene (experiments 2 - 4) suggest that the 2-methyltetrols are directly generated from intermediate C_5-alkene diols under the chamber conditions, likely as a result of RO_2 + RO_2 reactions on the generated C_5-trihydroxyperoxy radicals. In a more recent study, Paulot

Table 1. Concentrations of SOA tracers and of total SOA mass formed from irradiation reactions and percentage contributions.

Exp.	**SOA tracers in ng/m^3 (% of ∑tracers)**							**Total SOA mass (μg/m^3)**	**∑tracers % of total SOA mass**
	2-methylglyceric acid	C_5-alkenetriols	2-methylthreitol	2-methylerythritol	C_5-acids	C_5-diacids	∑ tracers		
1	0.18 (0.72)	11.7 (47)	3.7 (14.8)	9.1 (36)	-	-	25	-	-
2	11.4 (9.8)	8.0 (6.9)	29 (25)	53 (46)	13.4 (11.6)	1.33 (1.15)	116	19	0.6
3	18.0 (12.7)	23 (16.3)	34 (24)	55 (39)	10.2 (7.2)	1.34 (0.94)	142	4	3.5
5	79 (16.1)	-	167 (34)	230 (47)	14.2 (2.9)	4.3 (0.86)	490	27	1.83
7	5.9 (5.3)	-	23 (21)	79 (71)	2.5 (2.3)	0.69 (0.62)	111	3	3.7
8a	59 (6.1)	46 (4.7)	250 (26)	540 (56)	73 (7.5)	-	970	8	12.1
8b	-	-	42 (20)	168 (80)	-	-	210	2	10.5
9	3.4 (1.48)	-	63 (27)	154 (67)	12.2 (5.3)	1.81(0.79)	230	8	2.9
10a	55 (2.6)	8.7 (0.41)	640 (30)	1070 (51)	310 (14.8)	-	2100	5	42
10b	147 (3.9)	15.0 (0.39)	1310 (34)	2000 (53)	290 (7.6)	-	3800	27	13.9
10c	116 (5.5)	5.5 (0.26)	650 (31)	1100 (52)	210 (10.0)	-	2100	29	7.2
10d	87 (3.1)	10.9 (0.39)	890 (32)	1420 (51)	400 (14.3)	7.3 (0.26)	2800	25	11.3
10e	81 (4.3)	-	550 (29)	1170 (63)	73 (3.9)	-	1870	20	9.4
10f	17.9 (9.0)	-	59 (30)	109 (55)	9.1 (4.6)	4.9 (2.5)	200	8	2.5
11	8.6 (16.5)	-	9.4 (18.1)	34. (65)	-		52	3	1.73
12a	86 (3.2)	13.0 (0.48)	950 (35)	1590 (59)	30 (1.11)	-	2700	4	67
12b	116 (4.8)	12.5 (0.52)	780 (33)	1410 (59)	38 (1.58)	-	2400	15	15.7
12c	109 (6.9)	7.9 (0.50)	480 (30)	930 (58)	48 (3.0)	15.2 (0.96)	1590	13	12.2
12d	145 (8.5)	7.1 (0.42)	510 (30)	1000 (58)	45 (2.6)	3.7 (0.22)	1710	10	17.1
12e	88 (8.1)	9.8 (0.91)	330 (31)	620 (57)	28 (2.6)	3.0 (0.28)	1080	8	13.5
12f	12.1 (9.7)	-	33 (26)	75 (60)	3.6 (2.9)	1.65 (1.32)	125	1	12.5

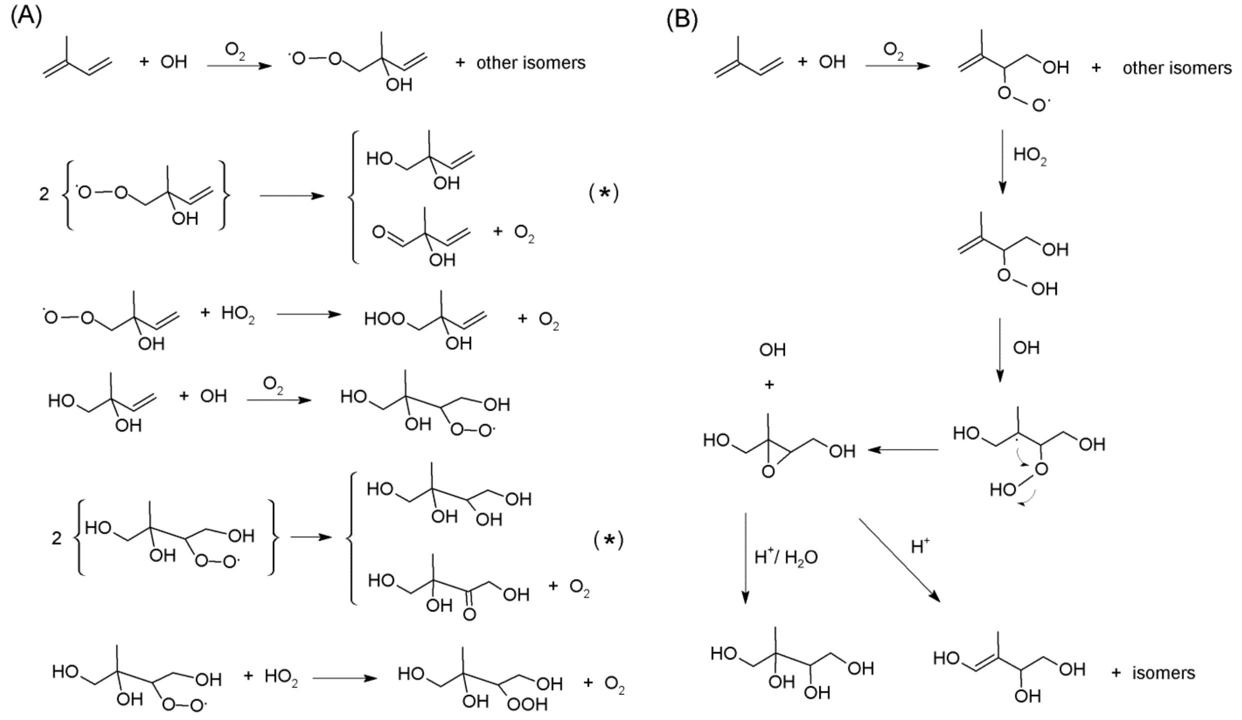
et al. (Paulot et al., 2009) detected gas-phase photooxidation products of isoprene with a molecular weight of 118, identified these products as isomeric C_5-epoxydiols and proposed them as gas-phase intermediates in the formation of the 2-methyltetrols and the C_5-alkene triols. A subsequent study by Surratt et al. (Surratt et al., 2010) confirmed that C_5-epoxydiols indeed serve as the intermediate gas-phase precursors for the 2-methyltetrols and C_5-alkene triols in the particle phase [Scheme 1(B)], as well as for C_5-epoxydiol dimers and organosulfates. Our efforts in the present study to detect C_5-epoxydiols in the gas phase upon photooxidation of isoprene (experiments 2 - 4) by a trapping experiment in acidified methanol failed; a possible explanation is that under our experimental conditions they are not formed as major gas-phase intermediates. An indication that they are produced as minor gas-phase intermediates serving as precursors for the 2-methyltetrols is that the C_5-alkene triols, which have been shown to be formed from C_5-epoxydiols (Paulot et al., 2009) are only generated at a rather low relative abundance [Fig. 1(B)].

Table 2. Percentage contributions of the SOA marker compounds to the total identified SOA mass and *threo*/*erythro* abundance ratios of 2-methyltetrol diastereoisomers. The data listed are averages per type of experiment (see text for details).

Experiments (n)[a]	**% of ∑(SOA)**							***threo/ erythro ratio***
	2-MG	C_5-alkene triols	2-MTs	C_5-acids	C_5-diacids	*threo*	*erythro*	
Isoprene/O_3 (1)	0.7	47	51	-	-	15	36	0.42
Isoprene/OH (2)	11	11	67	9.4	1.1	24	42	0.57
Diol 1/OH (1)	16	-	81	2.9	0.9	34	47	0.72
Diol 2/OH (2)	3.9	-	93	3.0	1.0	24	68	0.35
Diol 3/OH (1)	13	-	85	-	-	22	63	0.35

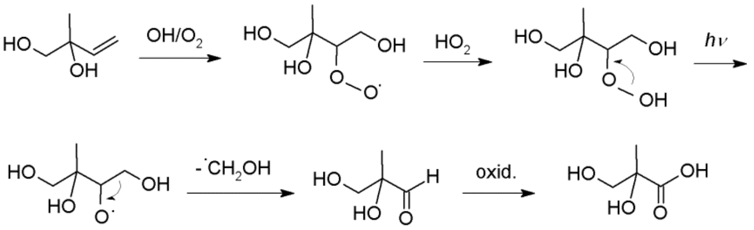
[a] number of experiments

It thus appears that our experimental conditions do not favor the formation of C_5-epoxydiols but lead to the formation of C_5-alkene diols, likely as a result of RO_2 + RO_2 reactions on the corresponding hydroperoxy radicals [Scheme 1(A)]. The observations, however, that the C_5-alkene diols have been detected in the ambient atmosphere and can readily be converted to 2-methyltetrols, as shown in the present study (Kleindienst et al., 2009), suggest that the route through C_5-alkene diol gas-phase intermediates could be a possible minor route leading to the 2-methyltetrols. On the basis of the *threo*/*erythro* abundance ratio of the 2-methyltetrols, it is, however, not possible to determine to which extent this route is followed; assuming that the isomeric C_5-alkene diols are produced in comparable amounts as shown by Kleindienst et al. (Kleindienst et al., 2009), the expected *threo*/*erythro* ratio is 0.44, very close to the ratio of 0.45 observed for ambient fine aerosol (Fig. 1). It is noted that the isoprene mixing ratios applied in our study (94 ppb) is lower than the lowest mixing ratios that were applied in the studies of Ruppert and Becker (Ruppert and Becker, 2000) (i.e., 1.86 ppm) and Kleindienst et al. (Kleindienst et al., 2009) (i.e., 8.7 ppm) for which C_5-alkene diols were detected, but somewhat higher than those of Paulot et al. (Paulot et al., 2009) (i.e., 20.9 ppb) and Surratt et al. (Surratt et al., 2010) (i.e., 40 ppb) for which C_5-epoxydiols and C_5-alkene triols, respectively, were reported. A notable difference, however, between the experimental conditions in the studies of Ruppert and Becker (Ruppert and Becker, 2000), Kleindienst et al. (Kleindienst et al., 2009) and our study and the studies of Paulot et al. (Paulot et al., 2009) and Surratt et al. (Surratt et al., 2010) is the way in which the H_2O_2 was introduced into the chamber; while H_2O_2 was continuously introduced in the first two studies and ours, a known mass of H_2O_2 was introduced in the beginning of the experiment (first 15-20 min) in the last two studies, likely giving rise to significant HO_2 radical levels by the OH + H_2O_2 reaction, which is favored at the slow chamber photolysis rate of H_2O_2. It is worth noting that the product distribution of isoprene SOA marker compounds obtained in the photolysis reaction of ozone [Fig. 1(C)] under more atmospherically relevant conditions in the presence of water vapor (RH 30%) is comparable to that obtained for ambient aerosol [Fig. 1(A)]; more specifically, the 2-methyltetrols and C_5-alkene triols show comparable relative abundances. A possible explanation is that photolysis of ozone in the presence of water vapor suppresses RO_2 + RO_2 reactions, but instead favors RO_2 + HO_2 reactions, thereby facilitating C_5-epoxydiol and subsequent 2-methyltetrol + C_5-alkene triol formation [Scheme 1(B)]. In this context, recent experiments in the gas phase by Berndt (Berndt, 2012) on the OH radical reaction of isoprene for low-NO_x conditions employing photolysis of ozone suggested a possible effect of water on the kinetics or the reaction mechanism. However, this new water-dependent gas-phase isoprene chemistry still needs to be explored in detail.



Scheme 1. Pathways reported for the formation of the 2-methyltetrols through photooxidation of isoprene: (A) pathway involving C_5-alkene diols as gas-phase intermediates (reproduced from Kleindienst et al., 2009); and (B) pathway involving C_5-epoxydiols as gas-phase intermediates (adapted from Surratt et al., 2010). The reactions marked with * are relevant to the current study.

As to the formation of 2-methylglyceric acid through photooxidation of isoprene, it has been shown that this marker compound is mainly formed in chamber experiments under high-NO_x conditions (Edney et al., 2005) and that it involves methacroylperoxynitrate (MPAN) and its subsequent oxidation product 2-methyloxirane-carboxylic acid as gas-phase intermediates (Surratt et al., 2010; Lin et al., 2013). The results obtained in the present study show that 2-methylglyceric acid is formed as a minor marker compound through photooxidation of isoprene at low NO_x conditions, and can also be produced from the C_5-alkene diols 1 and 3 under such conditions. It thus appears that there is a minor low-NO_x pathway operating in the formation of 2-methylgyceric acid. A possible pathway leading to the formation of 2-methylglyceric acid from diol 1 involving the photolysis of 2-hydroperoxy-1,3,4-trihydroxy-3-methylbutane is presented in Scheme 2. In this respect, it is worth mentioning that low atmospheric levels of 2-methylglyceric acid (on average 1.1 ng m^{-3}) have been measured in ambient fine aerosol collected during a 2004 summer episode at a boreal forest site, i.e., Hyytiälä, Finland (Kourtchev et al., 2005).



Scheme 2. Proposed pathway for the formation of 2-methylglyceric acid via the C_5-alkene diol 1,2-dihydroxy-2-methyl-3-butene (diol 1) under low-NO_x conditions.

Optimization of analytical methodology: LC/MS results

LC/MS measurements were performed with IP reagent being present both in the mobile phase and the reconstitution solution. The highest amount of each of the test compounds injected on column in a volume of 5 µL the molar excess of DBAA was more than 10^3 (i.e., 3.3×10^3, 4.1×10^3, 8.2×10^3, and 4×10^3 for 1.46 ng MSA, 1.34 ng ES, 0.75 ng PS, and 1.03 ng GS, respectively). Because a constant amount of IP reagent was present in the mobile phase as well as in the injection solution, no RT shift was observed when the injection volume was changed, as reported for the ion-pairing LC/MS analysis of an organophosphate drug metabolite (Zhao et al., 2013). To evaluate the sensitivity of the ion-pairing LC/MS method, standards at 7 concentrations spanning the range 0.002 ng – 1.5 ng mL^{-1} were prepared and an aliquot of 5 µL was injected. The test compounds could be detected with a S/N ratio of about 10 for an amount injected on column of 3.7 ng, 0.04 ng, 0.03 ng, and 0.02 ng, for MSA, ES, PS, and GS, respectively, demonstrating the sensitivity of the method.

Figure 2(A) shows selected LC/MS data obtained for a standard mixture (corresponding to 8.3 ng, 10.3 ng, 20.5 ng, and 10 ng injected on column for MSA, ES, PS, and GS, respectively), including a base peak chromatogram (BPC) and extraction ion chromatograms (EICs) at *m/z* 191, 109, 123, and 259, corresponding to an adduct ion of methanesulfonate (i.e., $CH_3SO_3H{:}CH_3SO_3^-$), ethanesulfonate, 2-propanesulfonate, and D-galactose 6-sulfate, respectively. It can be seen that ethanesulfonate (*m/z* 109) is also detected on the *m/z* 191 trace, owing to the formation of an adduct ion with sodium acetate (82 Da) which is present in the system (acetate is the anionic part of the IP reagent).

In a following step, the method was applied to an ambient aerosol sample, i.e., an extract of K-puszta fine aerosol containing polar organosulfates, which was investigated in detail in a recent study (Safi Shalamzari et al., 2013). Figure 2 presents the comparison of selected LC/MS data for K-puszta fine aerosol obtained with the developed ion-pairing method (B) and the method using the T3 column (C). BPCs and EICs at *m/z* 195, 215, 199, and 183 corresponding to sulfate and abundant OSs that are related to isoprene SOA are shown. It can be seen that the ion-pairing method provides better retention for the targeted OSs (i.e., OSs of 2-methyltetrols (*m/z* 215), 1,2-dihydrobutan-3-one (*m/z* 183), and 2-methylglyceric acid (*m/z* 199)) compared to the method based on the T3 column, where the 2-methyltetrol OSs are only partially separated from sulfate and 2-methylglyceric acid OS. Sulfate (RT 9.99 min) elutes as a broad tailing peak after the OSs of the 2-methyltetrols (*m/z* 215) (RTs 4.26 and 4.87 min), which are baseline-separated, and a 1,2-dihydroxy-3-butanone OS containing the sulfate group at the 1-position (*m/z* 183) (RT 5.51 min). Furthermore, a better chromatographic separation of *m/z* 199 OSs could be achieved compared to the T3 method with the major compound, 2-methylglyceric acid OS containing the sulfate group at the terminal position (RT 13.15 min) being separated from other isobaric *m/z* 199 compounds. This improved chromatographic separation enabled a more detailed mass spectral characterization of the 2-methyltetrol OSs and the characterization of a relatively abundant *m/z* 199 OS (RT 11.30 min) which could not be revealed with the T3 method, owing to co-elution.

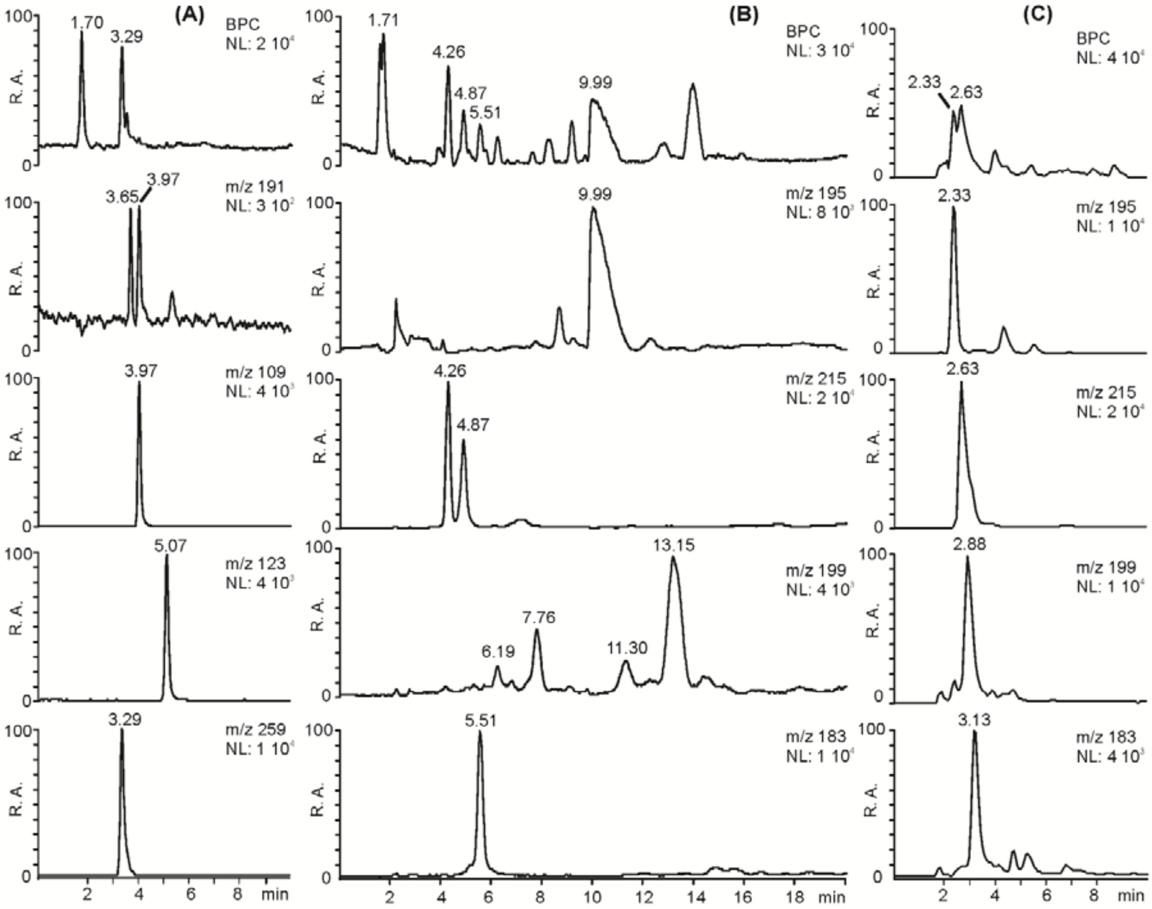


Figure 2. Selected LC/(−)ESI-MS chromatographic data (i.e., base peak chromatograms (BPCs) and extracted ion chromatograms (EICs)) for (A) a test mixture containing methanesulfonate (8.3 ng) (*m/z* 191), ethanesulfonate (10.3 ng) (*m/z* 109), 2-propylsulfonate (20.5 ng) (*m/z* 123), and D-galactose 6-sulfate (10 ng) (*m/z* 259) analyzed with the developed ion-pairing method; (B) K-puszta fine aerosol containing sulfate (*m/z* 195) and sulfate esters of 2-methyltetrols (*m/z* 215), 2-methylglyceric acid (*m/z* 199), and 1,2-dihydroxy-3-butanone (*m/z* 183) analyzed with the same ion-pairing method as for (A); and (C) the same K-puszta fine aerosol analyzed with a method previously reported using a C_{18} T3 column (Shalamzari et al., 2013). The *m/z* 199 compounds eluting at 6.19 and 7.76 min (B) were found not to correspond to OSs. Abbreviation: NL, normalization level.

Conclusions

Additional insights have been obtained on pathways leading to the formation of isoprene SOA marker compounds and the discrepant results reported in the literature for the underlying formation mechanisms, more specifically, with regard to the formation of the 2-methyltetrols which can either be explained by acid-catalyzed hydrolysis of C_5-epoxydiols or further photooxidation of C_5-alkene diols. We show that isomeric C_5-alkene diols serve as precursors for the 2-methyltetrols, i.e., 2-methylthreitol and 2-methylerythritol, under low-NO_x conditions, and rule out their involvement in the formation of the C_5-alkene triols. Furthermore, we demonstrate that there is a minor low-NO_x pathway leading to 2-methylglyceric acid, which may be relevant to ambient conditions.

An analytical methodology base on ion-pairing LC/(−)ESI-MS has been developed which allows an improved chromatographic separation of polar organosulfates.

References

Berndt T. Formation of carbonyls and hydroperoxyenals (HPALDs) from the OH radical reaction of isoprene for low-NOx conditions: influence of temperature and water vapour content. *J. Atmos. Chem*., 2012, **69**, 253–272.

Böge O., Miao Y., Plewka A. and Herrmann H. Formation of secondary organic particle phase compounds from isoprene gas-phase oxidation products: An aerosol chamber and field study. *Atmos. Environ.*, 2006, **40**, 2501–2509.

Claeys M., Graham B., Vas G., Wang W., Vermeylen R., Pashynska V., Cafmeyer J., Guyon P., Andreae M. O., Artaxo P. and Maenhaut W. Formation of secondary organic aerosols through photooxidation of isoprene. *Science*, 2004a, **303**, 1173–1176.

Claeys M., Wang W., Ion A. C., Kourtchev I., Gelencsér A. and Maenhaut W. Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide. *Atmos. Environ*., 2004b, **38**, 4093–4098.

Edney E.O., Kleindienst T.E., Jaoui M., Lewandowski M., Offenberg J. H., Wang W. and Claeys M. Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NOX/SO2/air mixtures and their detection in ambient PM2.5 samples collected in the eastern United States. *Atmos. Environ*., 2005, **39**, 5281–5289.

Gómez-González Y., Surratt J. D., Cuyckens F., Szmigielski R., Vermeylen R., Jaoui M., Lewandowski M., Offenberg J. H., Kleindienst T. E., Edney E. O., Blockhuys F., Van Alsenoy C., Maenhaut W., Claeys M. Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-)electrospray ionization mass spectrometry. *J. Mass Spectrom*. **2008**, *43*, 371–382.

Grechkin A. N., Mukhtarova L. S. and Hamberg M. Thermal conversions of trimethylsilyl peroxides of linoleic and linolenic acids. *Chem. Phys. Lipids*, 2005, **138**, 93–101.

Guenther A., Hewitt C. N., Erickson D., Fall R., Geron C., Graedel T., Harley P., Klinger L., Lerdau M., Mckay W. A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J., and Zimmerman P. A global model of natural volatile organic compound emissions. *J. Geophys. Res.*, 1995, **100**, 8873–8892.

Hodgson D. M., Stent M. A. H. and Wilson F. X. Substituted alkenediols by alkylative double ring opening of dihydrofuran and dihydropyran epoxides. *Org. Lett*., 2001, **3**, 3401–3403.

Iinuma Y., Böge O., Keywood M., Gnauk T. and Herrmann H. Atmospheric tracers for secondary organic aerosol formation from 1,8-cineole oxidation. *Environ. Sci. Technol*., 2009, **43**, 280–285.

Kleindienst T. E., Lewandowski M., Offenberg J. H., Jaoui M. and Edney E. O. The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NOx *Atmos. Environ*., 2009, **9**, 6541–6558.

Kourtchev I., Ruuskanen T., Maenhaut W., Kulmala M. and Claeys M. Observation of 2-methyltetrols and related photooxidation products of isoprene in boreal forest aerosols from Hyytiälä. *Atmos. Chem. Phys.*, 2005, **5**, 2761–2770.

Lin Y.-H., Zhang H., Pye H. O. T., Zhang Z., Marth W. J., Park S., Arashiro M., Cui T., Budisulistiorini S. H., Sexton K. G., Vizuete W., Xie Y., Luecken D. J., Piletic I. R., Edney E. O., Bartolotti L. J., Gold A. and Surratt J. D. Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides. *Proc. Natl. Acad. Sci.* USA, 2013, doi/10.1073/pnas.1221150110.

Maenhaut W., Raes N., Chi X., Cafmeyer J. and Wang W. Chemical composition and mass closure for PM2.5 and PM10 aerosols at K-puszta, Hungary, in summer 2006. *X-Ray Spectrom.* 2008, **37**, 193–197.

Miyoshi A., Hatakeyama S. and Washida N. OH radical- initiated photooxidation of isoprene: An estimate of global CO production. *J. Geophys. Res*., 1994, **99**,18779–18787.

Pashynska V., Vermeylen R., Vas G., Maenhaut W. and Claeys M. Development of a gas chromatography/ion trap mass spectrometry method for determination of levoglucosan and saccharidic compounds in atmospheric aerosols: Application to urban aerosols. *J. Mass Spectrom*., 2002, **37**, 1249–1257.

Paulot F., Crounse J. D., Kjaergaard H. G., Kürten A., St. Clair J. M., Seinfeld J. H. and Wennberg P. O. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science*, 2009, **325**, 730–733.

Ruppert L. and Becker K. H. A product study of the OH radical initiated oxidation of isoprene: formation of C5-unsaturated diols *Atmos. Environ*., 2000, **34**, 1529–1542.

Shalamzari M. S., Ryabtsova O., Kahnt A., Vermeylen R., Hérent M.-F., Quetin-Leclercq J., Van der Veken P., Maenhaut W., Claeys M. Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene. *Rapid Commun. Mass Spectrom.* **2013**, *27*, 784–794.

Surratt J. D., Murphy S. M., Kroll J. H., Ng N. L., Hildebrandt L., Sorooshian A., Szmigielski R., Vermeylen R., Maenhaut W., Claeys M., Flagan R. C. and Seinfeld J. H. Chemical compositon of secondary organic aerosol formed the photooxidation of isoprene. *J. Phys. Chem*. A, 2006, **110**, 9665–9690.

Surratt J. D., Chan A. W. H., Eddingsaas N. C., Chan M. N., Loza C. L., Kwan A. J., Hersey S. P., Flagan R. C., Wennberg P. O. and Seinfeld J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc. Natl. Acad. Sci.* USA, 2010, **107**, 6640–6645.

Wang W., Kourtchev I., Graham B., Cafmeyer J., Maenhaut W. and Claeys M. Characterization of oxygenated derivatives of isoprene related to 2-methytetrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass spectrometry. *Rapid Commun. Mass Spectrom*., 2005, **19**, 1343–1351.

Zhao Y., Liu G., Liu Y., Yuan L., Hawthorne D., Shen J. X., Guha M., Aubry A. Improved ruggedness of an ion-pairing liquid chromatography/tandem mass spectrometry assay for the quantitative analysis of the triphosphate metabolite of a nucleoside reverse transcriptase inhibitor in peripheral blood mononuclear cells. *Rapid Commun. Mass Spectrom.* **2013**, *27*, 481–488.

Publications in peer-reviewed international journals

- Wu Wang, Mohammad Safi Shalamzari, Willy Maenhaut, Magda Claeys. Ion-pairing liquid chromatography/negative ion mass spectrometry for improved analysis of polar isoprene-related organosulfates. Rapid Commun. Mass Spectrom. 2013, 27, 1585–1589
- Wu Wang, Yoshiteru Iinuma, Ariane Kahnt, Oxana Ryabtsova, Anke Mutzel, Reinhilde Vermeylen, Pieter Van der Veken, Willy Maenhaut, Hartmut Herrmann*,* Magda Claeys. Formation of secondary organic aerosol marker compounds from the photooxidation of isoprene and isoprene-derived alkene diols under low-NO_x conditions. Faraday Discuss. 165, 261-272, 2013.