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Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/ NO_X/SO_2 /air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States

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Abstract

Recent observations in ambient PM_{2.5} of 2-methylthreitol, 2-methylerythritol and 2-methylglyceric acid, proposed isoprene oxidation products, suggest the contribution of isoprene to SOA formation, long thought to be relatively unimportant, should be reexamined. To address this issue, an isoprene/ NO_X /air mixture was irradiated in a flow reactor smog chamber in both the absence and presence of SO₂ to measure the SOA yield of isoprene and to establish whether the two 2-methyl tetrols and 2-methylglyceric acid are present in isoprene SOA and could serve as SOA indicator compounds. In the absence of SO₂, the SOA yield of 0.002 was low, as expected, although uncertain because the SOA concentration was near chamber background levels. However, in the presence of SO₂, the SOA yield increased significantly to 0.028. Analysis of the trimethylsilyl derivatives of the SOA samples by gas chromatography/mass spectrometry showed chamber concentrations of the two 2-methyl tetrols totaling $0.1\,\mu\mathrm{g\,m^{-3}}$ and a 2-methylglyceric acid concentration of $0.4 \,\mu\mathrm{g}\,\mathrm{m}^{-3}$ in the absence of SO_2 , with the levels increasing significantly to $6.3 \,\mu\mathrm{g}\,\mathrm{m}^{-3}$ and $1.2 \,\mu\mathrm{g}\,\mathrm{m}^{-3}$, respectively, when SO_2 was added. The laboratory data suggest that these compounds are possible indicator compounds for isoprene SOA and that the presence of SO2 enhances significantly SOA formation from isoprene photooxidation, with acid-catalyzed reactions possibly playing a major role. The importance of these findings was supported by the detection of the two 2-methyl tetrols and 2-methylglyceric acid in summertime ambient PM_{2.5} samples collected at three locations in the eastern United States. However, additional mechanistic studies are required to predict the contributions of the SO₂-assisted isoprene SOA formation to ambient PM_{2.5} concentrations. © 2005 Elsevier Ltd. All rights reserved.

Keywords: PM_{2.5}; Secondary organic aerosol; Isoprene; Acid-catalyzed reactions; 2-methylthreitol; 2-methylerythritol; 2-methylglyceric acid

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1. Introduction

Particulate matter with aerodynamic diameters less than 2.5 µm (PM_{2.5}), formed from direct emissions and through secondary processes, can adversely affect visibility, the climate, and human health. To reduce these impacts, the major sources of PM_{2.5} must be identified and control strategies are required to reduce their ambient concentrations. While primary emissions of $PM_{2.5}$ containing NO_X and SO_X compounds, along with secondary inorganic aerosol formation pathways involving radical-driven gas-phase reactions of SO₂ and NO₂, are reasonably well understood, considerable uncertainty remains surrounding direct emissions and secondary processes controlling ambient concentrations and compositions of the organic fraction of PM_{2.5}. Major primary sources of organic aerosol include gasoline exhaust and diesel emissions from on-road and off-road vehicles, natural gas combustion, meat cooking operations, road dust, vegetative detritus, and biomass burning (Zheng et al., 2002). Ambient organic aerosol concentrations are also affected by secondary organic aerosol (SOA) formation through atmospheric reactions of volatile hydrocarbons forming semivolatile and nonvolatile compounds that are subject to nucleation reactions and absorption and/or adsorption onto existing PM_{2.5}, and possible further reactions in the aerosol to form oligomers. There is a general consensus in the atmospheric chemistry community that monoterpenes, aromatic hydrocarbons, and possibly sesquiterpenes are significant contributors to SOA, while the contribution from isoprene has been generally thought to be negligible based on the arguments put forth by Pandis et al. (1991). However, within the past 2 years, evidence from both field and laboratory experiments has been presented for isoprene contributing to SOA formation. During the July 2001 LBA-CLAIRE wet season campaign in the Amazonian rainforest in Balbina, Brazil, Claeys et al. (2004a) identified the two diastereoisomeric 2-methyl tetrols, 2-methylthreitol and 2-methylerythritol, in ambient PM_{2.5} samples. The total 2-methyl tetrol concentration was $49 \, \mathrm{ng} \, \mathrm{m}^{-3}$ during the day and 65 ng m⁻³ at night. Based on the presence of the isoprene skeleton in these highly polar nonvolatile compounds and the high emission rates of isoprene, Claevs and co-workers proposed the two 2-methyl tetrols could form by gas-phase atmospheric reactions of isoprene and contribute to SOA formation by condensing onto existing PM_{2.5}. More recently, they observed 2-methylthreitol and 2-methylerythritol concentrations in ambient PM_{2.5} in a mixed deciduous/ coniferous forest at K-puszta, Hungary, ranging from 1 to 34 ng m^{-3} and 1 to 85 ng m^{-3} , respectively, during the summer of 2003 (Ion et al., 2005). In this same study, the polar oxygenated compound 2-methylglyceric acid was observed in PM_{2.5} at ambient concentrations ranging between 2 ng m^{-3} and 18 ng m^{-3} . In a subsequent study, they synthesized each of the three compounds in the laboratory by reacting hydrogen peroxide (H₂O₂) and H₂SO₄ in aqueous solutions with (1) isoprene to form the two 2-methyl tetrols and (2) the isoprene oxidation products methacrolein and methacrylic acid to form 2methylglyceric acid (Claevs et al., 2004b). The results of the syntheses led Claeys and co-workers to propose the three polar compounds could form in the troposphere by uptake of their organic precursors into acidified PM_{2.5}, followed by reaction with H₂O₂. Other recent studies supporting isoprene's contribution to the organic fraction of ambient PM_{2.5} are the laboratory investigations carried out by Jang et al. (2002), who found evidence that the presence of acidic seed aerosol catalyzed the SOA-forming ozonolysis reaction of isoprene, and Limbeck et al. (2003), who showed the exposure of quartz filters impregnated with H₂SO₄ to gas-phase isoprene led to the formation of polymers on the filters.

To investigate the role of the two 2-methyl tetrols and 2-methylglyceric acid in SOA formation from isoprene under more atmospherically relevant laboratory conditions, we have carried out a two-part laboratory experiment using a flow reactor smog chamber to irradiate isoprene/NO_X/air mixtures, in both the presence and absence of SO₂. Polar oxidation products in the SOA were derivatized to their trimethylsilyl derivatives and analyzed by gas chromatography/ion trap mass spectrometry in the electron ionization mode. The laboratory results were compared with the chemical composition of the polar organic fraction of PM_{2.5} collected during the summer of 2001 in Research Triangle Park, North Carolina, Baltimore, Maryland, and Philadelphia, Pennsylvania.

2. Photooxidation experiments

To generate laboratory filter samples with a sufficient quantity of SOA from irradiated isoprene/NO_X/air mixtures in the absence and presence of SO₂, a twopart experiment was carried out by operating a smog chamber in a dynamic mode, which allowed continuous filter sampling for extended periods while the aerosol concentrations in the chamber were at constant steadystate concentrations. The experiments were conducted in a 14.5 m³ smog chamber that has a rectangular design and is fabricated from stainless steel with interior walls covered with a 0.038-mm TFE Teflon coating. The chamber is equipped with four banks of fluorescent bulbs (40 bulbs per bank) that provide radiation distributed over the UV portion of the spectrum from 300 to 400 nm. The irradiation source is based on a combination of UVA-340 bulbs (Q-Panel, Cleveland, OH) and standard UV bulbs (GE F40-BL) that provide

radiation between 300 and 340 nm and 340 and 400 nm, respectively. The NO₂ photolysis rate for these experiments was approximately 0.34 min⁻¹.

The dynamic mode of operation required continuous addition of reactants through a mixing manifold into the chamber. The dilution airflow was $0.040\, m^3\, min^{-1}$, which gives a residence time of 6 h, for gases in the chamber. NO and SO_2 (each 1% in N_2) and isoprene (0.15% in $N_2)$ were injected from high pressure cylinders using mass flow controllers. Ammonium sulfate seed aerosol, at a resultant concentration less than $1\,\mu g\,m^{-3}$, was added continuously into the chamber by nebulizing a $0.5\,mg\,L^{-1}$ aqueous ammonium sulfate solution. The relative humidity was maintained at a constant value of 30% with a computer-controlled peristaltic pump coupled to a high-temperature vaporizer to add water vapor to the chamber. The measured chamber temperature was $29.7\,^{\circ}C$ during the irradiation.

Selected chemical and physical parameters were monitored continuously during the experiments. NO and NO_X were measured with a TECO model 42C (Franklin, MA) oxides of nitrogen chemiluminescent analyzer; SO₂ was monitored by pulsed fluorescence detection (TECO, Model 43A) and O3 was monitored with a conventional ozone moniter (Bendix Model 8002, Lewisburg, WV). Inlet manifold and chamber isoprene concentrations were measured using a cryogenic trap for sample collection with analysis by gas chromatography with flame ionization detection (Hewlett Packard, Model 5890 GC). Gas-phase carbonyl products were measured by bubbling the chamber effluent through an acidified solution of 2,4-dinitrophenyl-hydrazine. The hydrazone derivatives were separated by reverse-phase liquid chromatography and analyzed by UV detection (LDC/Milton Roy CM4000 Liquid Chromatograph). The temperature and relative humidity during the irradiation were monitored with an Omega Thermo-Hydrometer (Model RH411).

SOA compounds produced during the reaction were collected with several types of filters depending on the specific chemical analysis. Inorganic compositions were determined by collecting chamber aerosol on a 47-mm, 0.45-µm Teflon filter. Teflon filter de-ionized water extracts were analyzed for their ionic contents by ion chromatography with a DX500 Dionex Ion Chromatograph System equipped with an electrical conductivity detector. Cation analysis was performed with a Dionex IonPac CS15 column and an isocratic 9% acetonitrile/ 10 mN sulfuric acid eluent. Anion analysis was conducted using a Dionex IonPac AS14A column and an isocratic 4 mM sodium carbonate/0.5 mM sodium bicarbonate eluent. Samples for total organic carbon were collected with a graphite carbon strip denuder, with an extremely high capacity for gas-phase carbon absorption, followed by two quartz-fiber filters, with the back filter used to only partially correct for evaporative losses since the collection efficiency for gas phase carbon compounds is less than 100%. The filter samples were analyzed by the thermal-optical method developed by Birch and Cary (1996). Samples for determining the mass and composition of the polar organic fraction of SOA were collected with an XAD-4 denuder followed by a glass-fiber filter. The chamber background concentrations for the aerosol mass and aerosol OC concentrations were $1.9\pm1.1\,\mu\mathrm{g\,m^{-3}}$ and $1.8\pm0.9\,\mu\mathrm{g\,m^{-3}}$, respectively, whereas chamber wall loss rates were $0.17\%\ h^{-1}$ for SO₂, $6.3\%\ h^{-1}$ for SOA obtained by irradiating a mixture of toluene and α -pinene in the presence of NO_X and $7.5\%\ h^{-1}$ for an acidic aerosol generated by nebulizing a 1:1 ammonium sulfate—sulfuric acid aqueous mixture.

Polar organic compounds were characterized after conversion to their trimethylsilyl derivatives by gas chromatography/mass spectrometry (GC/MS) in the electron ionization and full-scan modes with a Trace GC2000 gas chromatograph/Polaris Q ion trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA). A part of the filter (1/16) was extracted with dichloromethane:methanol (4:1, v/v). A detailed description of the sample workup procedure and the GC/MS instrumental conditions have been reported elsewhere (Pashynska et al., 2002). The following GC temperature program was applied: the initial temperature of 50 °C was kept for 5 min; subsequently, the temperature was increased to 200 °C at a rate of 3 °C min⁻¹ and kept at that temperature for 2 more min, and then raised to 310 °C at a rate of 30 °C min⁻¹. The total analysis time was 62 min. An aliquot (1/40) of the trimethylsilylated aerosol extract from the experiment with SO₂ was injected in the split mode (split ratio 1/50), while that from the experiment without SO2 was injected in the splitless mode (Fig. 1). Quantitative determination of the two 2-methyl tetrols, 2-methylthreitol and 2-methylerythritol, and 2-methylglyceric acid (2,3-dihydroxy-2methylpropanoic acid, also denoted by 2,3-dihydroxymethacrylic acid in previous work [Claeys et al., 2004b]) was performed by GC with flame ionization detection with a GC 8000 Top instrument (Carlo Erba, Milan, Italy). A part of the filter (1/16) was spiked with internal recovery standards in amounts comparable (within 10-fold range) to those of the measured compounds. The internal recovery standards were structurally related to the measured compounds: deuterated (d_3 -) malic acid (Cambridge Isotope Laboratories, Andover, MA, USA) was used for 2methylglyceric acid, while threitol and erythritol (both from Sigma, St. Louis, MO, USA) were used for 2methylthreitol and 2-methylerythritol, respectively. It was assumed that the GC-FID responses of the trimethylsilyl derivatives of the compounds and their respective internal standards were similar. Since the ionization efficiencies in GC-FID are roughly propor-

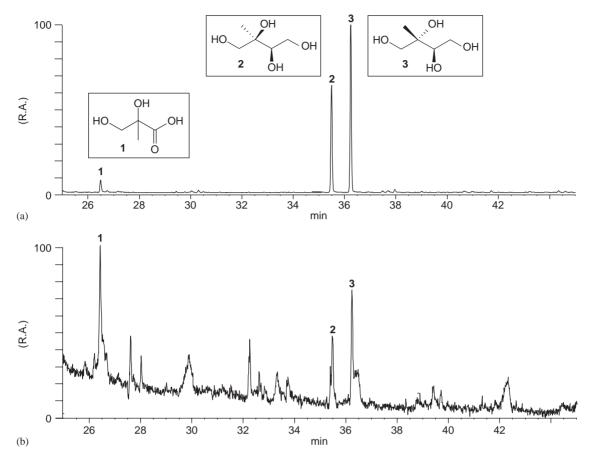


Fig. 1. GC/MS total ion chromatograms of trimethylsilylated derivatives obtained for the irradiated isoprene/ NO_X /air mixtures (a) in the presence and (b) absence of SO_2 . Peak identifications: (1) 2-methylglyceric acid, (2) 2-methylthreitol, and (3) 2-methylerythritol (structures shown in insets).

tional with the weight percent of the carbon atoms in the molecules (Ackman, 1964), the differences in the FID responses of the trimethylsilylated derivatives of the 2-methyl tetrols, 2-methylthreitol and 2-methylerythritol, and their internal standards, threitol and erythritol, respectively, (weight percent: 46.8 versus 45.3%) as well as those of 2-methylglyceric acid and its respective internal standard, deuterated malic acid, (weight percent: 46.4 versus 38.8%) can be neglected, given that they are much smaller than the precision of the measurements which is about 10%.

The chamber experiment was conducted in two stages. The initial concentrations for each stage are given in Table 1. In Part I, a mixture of 1680 ppbv isoprene, 629 ppbv NO_X, and 268 ppbv SO₂ in one atmosphere of air was first added continuously to the chamber. The lights were then turned on and the irradiated mixture was allowed to come to steady state in the chamber. With a constant composition maintained at steady state, gas-phase and aerosol-phase samples were collected. In Part II, SO₂ was removed from the reactant mixture,

Table 1 Initial concentrations in ppbv for the two-part experiment to determine SOA compounds from the isoprene photooxidation

Experiment	Isoprene	NO_X	NO^a	SO_2
I	1680	629	647	268
II	1610	627	648	< 1

^aThe apparent NO concentration being larger than NO_X is attributed to interfering chemiluminescence produced from ozone+isoprene reaction.

and the reactant concentrations were left essentially the same as those in Part I, as shown in Table 1. The mixture was again allowed to come to steady-state conditions and an identical set of gas-phase and aerosol-phase samples was collected in the absence of SO₂. For the U.S. field samples described below, the workup procedure and the chromatographic conditions were the same as those used for characterization by GC/MS

above, except that a more polar solvent system, dichloromethane:methanol (1:1, v/v), was used for extraction.

3. Results and discussion

The steady-state gas-phase and aerosol-phase concentrations for Parts I and II are summarized in Table 2. Major gas-phase organic oxidation products detected in the two highly oxidized mixtures, each containing about 370 ppbv O₃, were formaldehyde, acetaldehyde, propionaldehyde, acrolein, methyl vinyl ketone, methacrolein, glyoxal, and methyl glyoxal. With the exception of formaldehyde, the concentrations of the gas-phase oxidation products and the amounts of isoprene reacted were similar for the two irradiations. In the presence of SO₂, the gravimetrically determined aerosol mass concentration was $172.9 \,\mu\text{g}\,\text{m}^{-3}$ and included $42.8 \,\mu\text{g}\,\text{m}^{-3}$ OC, $45.0 \,\mu\text{g}\,\text{m}^{-3}$ SO₄² and $2.7 \,\mu\text{g}\,\text{m}^{-3}$ NH₄⁺, each of which has been corrected for the chamber background concentration and wall loss. The aerosol SO₄²⁻ was largely the result of gas-phase oxidation of SO₂ forming H₂SO₄ that readily condensed on the chamber aerosol. Analyses of the SO_2 and SO_4^{2-} data showed the amount of S lost by reaction of SO2 exceeded significantly that detected as SO_4^{2-} in the aerosol (149 vs. $15 \,\mu g \, m^{-3} \, S$), raising the possibility of significant levels of undetected

Table 2 Steady-state concentrations of gas-phase and aerosol-phase compounds

Compound	Part I (w/SO ₂)	Part II (w/o SO ₂)		
Gas-phase concentrations (ppb)				
Isoprene	70	50		
NO_Y	247	269		
NO	32	32		
SO_2	154	<1		
O_3	368	376		
Formaldehyde	798	1119		
Acetaldehyde	30	27		
Acrolein	14	12		
Propionaldehyde	16	20		
Methacrolein	105	88		
Methyl vinyl	71	63		
ketone				
Glyoxal	62	53		
Methyl glyoxal	224	219		
Aerosol-phase concentrations ^(a) (μg m ⁻³)				
Mass	172.9	7.8		
SO_4^{2-}	45.0	<1		
NH ₄ ⁺	2.7	<1		
OC	42.7	6.3		

^aAll aerosol concentrations have been corrected for chamber background concentrations and chamber wall losses.

organic sulfur compounds predominately in the gas phase, since such compounds in the aerosol phase would have been readily detected by the OC analyzer. Based on the findings of Niki et al. (1977), Finlayson–Pitts and Pitts (1986) proposed that the *cis*-2-butene Criegee intermediate could react with SO₂ forming S-bearing organic oxidation products. A similar reaction involving isoprene could be occurring in our system, which would help explain this discrepancy. This hypothesis is also supported by the significantly higher gas-phase formal-dehyde concentrations observed in the absence of SO₂ displayed in Table 2 which are consistent with organic sulfur compounds formed in the presence of SO₂ serving as sinks for formaldehyde and its precursors.

The calculated mass and molar concentrations for $H^+,$ based on a charge balance for the $H^+-NH_4^+-SO_4^{2-}$ system, were $0.8\,\mu g\,m^{-3}$ and $0.8\,\mu mol\,m^{-3},$ respectively, with a molar NH₄⁺ to SO₄² ratio of 0.3, the latter results consistent with the presence of an acidified aerosol. Based on an overall mass balance for the aerosol, the SOA concentration, which included in addition to OC contributions from nitrogen, hydrogen, oxygen, and possibly sulfur, was $124.4 \,\mu g \, m^{-3}$. The SOA to OC mass ratio was 2.9, a ratio that appears high compared with typical ratios of 1.9–2 experimentally estimated for rural PM_{2.5} aerosol at K-puszta, Hungary, by Kiss et al. (2002) and the ratio of 2.1 ± 0.2 suggested for non-urban PM_{2.5} aerosol by Turpin and Lim (2001). These high values may provide some evidence for sulfur compounds in the SOA not detected by ion chromatography. As shown in Table 2, in the absence of SO₂, the aerosol mass and OC concentrations decreased significantly to 7.8 and $6.3 \,\mu\mathrm{g}\,\mathrm{m}^{-3}$, respectively. The effective massbased SOA yield for isoprene, a common measure of the contribution of a hydrocarbon to SOA formation that is equal to [SOA]/[Isoprene], was 0.028 in the presence of SO₂, decreasing to 0.002 in the absence of SO₂. However, the latter result is uncertain because of the proximity of the SOA concentration to typical chamber aerosol mass background levels of $1.9 \pm 1.1 \,\mu \mathrm{g \, m^{-3}}$. Although the finding of the SOA yield increasing by a multiplicative factor of 14 in the presence of SO₂ is based on the results of just two experiments, it is important to note these results are further supported by another more recent study in our laboratory where the impact of SO₂ on the SOA yields of both isoprene and the monoterpene, α-pinene, was systematically investigated as a function of SO₂ concentrations (Kleindienst et al., 2005, submitted).

Further information on SOA formation from isoprene was provided by analyses of the total ion chromatograms (TICs) of the laboratory aerosol extracts (Fig. 1) containing trimethylsilylated derivatives of polar SOA compounds with alcoholic groups (–OH) and carboxylic acid groups (–C(O)OH). The polar organic compounds 2-methylglyceric acid and the two 2-methyl

tetrols, 2-methylthreitol and 2-methylerythritol, detected in the irradiated isoprene/ NO_X /air mixtures in both the absence and presence of SO_2 are shown in Fig. 1. While a high-quality TIC could be obtained for the experiment in the presence of SO_2 , peaks with a much lower signal-to-noise ratio (about 10/1 for 2-methylthreitol) and interferences were observed in the TIC of the experiment in the absence of SO_2 . The compounds were identified by comparing their electron ionization mass spectra

displayed in Fig. 2 with reference spectra for the compounds reported by Claeys et al. (2004b). A detailed study of the complex fragmentation behaviors of the trimethylsilyl derivatives of the two 2-methyl tetrols, 2-methylthreitol and 2-methylerythritol, in both the electron and methane chemical ionization modes is presented in Wang et al. (2004). In the absence of SO_2 , the mass concentrations of 0.4, <0.1, and 0.1 μ g m⁻³ for 2-methylglyceric acid and the two

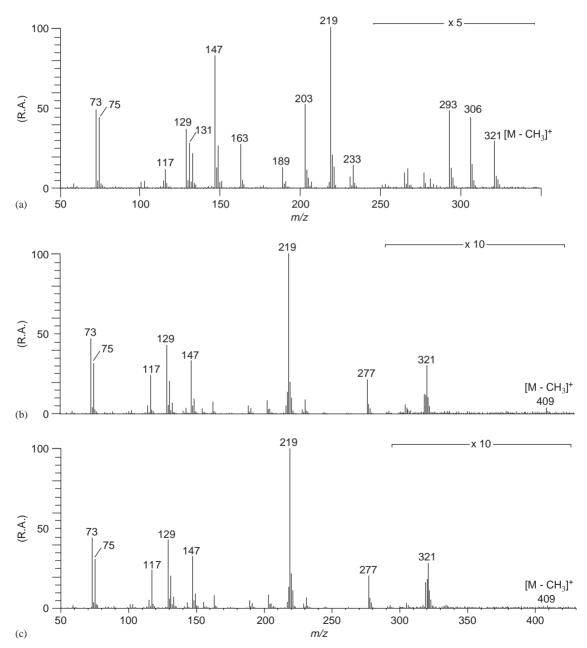


Fig. 2. Electron ionization ion trap mass spectra obtained for (a) peak 1,(b) peak 2, and (c) peak 3 shown in Fig. 1, which were identified as 2-methylglyceric acid, 2-methylthreitol, and 2-methylerythritol, respectively.

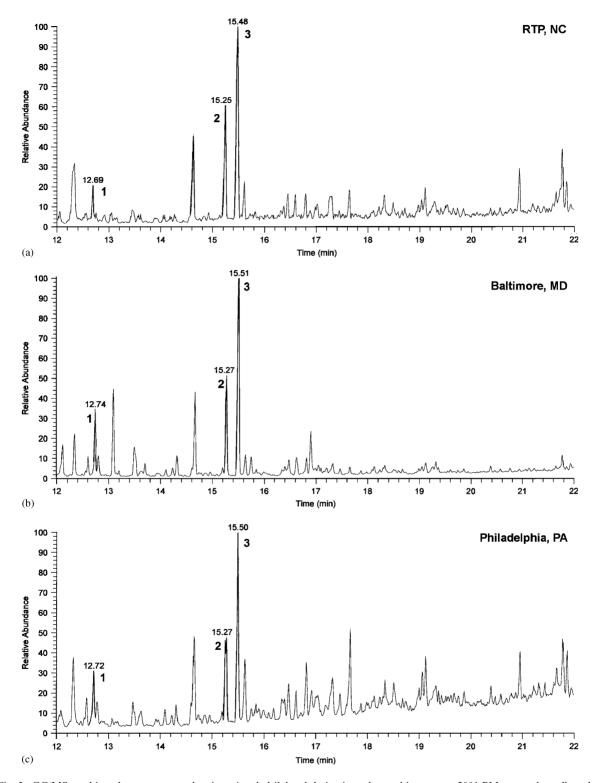


Fig. 3. GC/MS total ion chromatograms showing trimethylsilylated derivatives observed in summer 2001 $PM_{2.5}$ samples collected at (a) a suburban site in Research Triangle Park, North Carolina; (b) an urban site in Baltimore, Maryland; and (c) an urban site in Philadelphia, Pennsylvania. Peak identifications: (1) 2-methylglyceric acid, (2) 2-methylthreitol, and (3) 2-methylerythritol. (Chromatographic conditions were different from those described in Section 2.)

2-methyl tetrols, 2-methylthreitol and 2-methylerythritol, respectively, were low; however, in the presence of SO₂, the respective concentrations increased significantly to 1.2, 2.4, and $3.9 \,\mu \mathrm{g \, m}^{-3}$. The three polar compounds made up about 6% of the SOA in the presence of SO₂. The remaining SOA likely includes high molecular weight compounds that are not detected with our current instrumentation, including humic-like substances, which have been reported for the heterogeneous reaction of isoprene on acidic particles by Limbeck et al. (2003) and have been identified in ambient particulate matter (e.g., Havers et al., 1998; Krivacsy et al., 2001) as well as proposed as reaction products of acid-catalyzed reactions of isoprene oxidation occurring in the aerosol (Jang and Kamens, 2001; Jang et al., 2002; Matsunaga et al., 2003). In addition, only very recently, Liggio et al., 2005 reported that the reactive uptake of glyoxal, an isoprene oxidation product, into ammonium sulfate and mixed ammonium sulfate-sulfuric acid aqueous aerosols can lead to the formation of high molecular weight, low volatility, glyoxal adducts, some in the form of organic sulfates.

The atmospheric relevance of the laboratory observations is further supported by the detection of the three compounds in summer ambient PM2.5 samples collected in forested areas in Brazil and Hungary as cited earlier. The methyl tetrols contributed to the OC as much as 2% in the Brazil samples (Claeys et al., 2004a), while Ion et al. (2005) reported contributions as large as 1% in the Hungarian samples. Finally, additional data collected in the United States are provided in the TICs displayed in Fig. 3. These show the presence of trimethylsilylated derivatives of the three compounds observed in ambient summer PM_{2.5} samples we collected in the eastern United States at a suburban field site in Research Triangle Park, North Carolina and at urban field sites in Baltimore, Maryland, and Philadelphia, Pennsylvania, during 2001 (T.E. Kleindienst, unpublished results).

4. Conclusions

As far as we are aware, to date, isoprene and its oxidation products are the only proposed tropospheric precursors for the two 2-methyl tetrols and 2-methylglyceric acid detected in aerosols in our laboratory chamber and in $PM_{2.5}$ samples collected at field locations in North America, South America, and Europe. While our laboratory data show limited SOA formation from the irradiation of isoprene in the presence of NO_X , the yield increased significantly to 0.028 when SO_2 was added to the mixture. These data indicate that, under ambient daytime conditions in the summertime, the presence of isoprene and SO_2 along with typical tropospheric oxidants including OH, O_3 , and H_2O_2 could lead to SOA formation, with

 $\rm H_2SO_4$ -catalyzed reactions possibly playing a role. Furthermore, the GC/MS results suggest that the two 2-methyl tetrols and possibly 2-methylglyceric acid identified in both our laboratory and field samples could serve as indicator compounds for SOA from isoprene. The limited data, however, were insufficient to establish the $\rm SO_2$ -assisted SOA formation mechanism, and without such information the laboratory results cannot be extrapolated to ambient conditions. Additional research is currently underway in our laboratory to further clarify whether the processes occurring in the chamber are significant contributors to SOA formation under ambient conditions and whether there are additional sources of the two 2-methyl tetrols and 2-methylglyceric acid .

5. Disclaimer

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