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The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NO_x

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Abstract. The reaction of isoprene (C_5H_8) with hydroxyl radicals has been studied in the absence of nitrogen oxides (NO_x) to determine physical and chemical characteristics of the secondary organic aerosol formed. Experiments were conducted using a smog chamber operated in a steady-state mode permitting measurements of moderately low aerosol levels. GC-MS analysis was conducted to measure methyl butenediols in the gas phase and polyols in the aerosol phase. Analyses were made to obtain several bulk aerosol parameters from the reaction including values for the organic mass to organic carbon ratio, the effective enthalpy of vaporization (ΔH_{vap}^{eff}), organic peroxide fraction, and the aerosol yield.

The gas phase analysis showed the presence of methacrolein, methyl vinyl ketone, and four isomers of the methyl butenediols. These gas-phase compounds may serve as precursors for one or more of several compounds detected in the aerosol phase including 2-methylglyceric acid, three 2-methyl alkenetriols, and two 2-methyl tetrols. In contrast to most previous studies, the 2-methyl tetrols (and the 2-methyl alkenetriols) were found to form in the absence of acidic sulfate aerosol. However, reaction conditions did not favor the production of HO_2 radicals, thus allowing RO_2+RO_2 reactions to proceed more readily than if higher HO_2 levels had been generated.

SOA/SOC (i.e. OM/OC) was found to average 1.9 in the absence of NO_x. The effective enthalpy of vaporization was measured as 38.6 $\mathrm{kJ\,mol^{-1}}$, consistent with values used previously in modeling studies. The yields in this work (using an independent technique than used previously) are lower than those of Kroll et al. (2006) for similar aerosol masses. SOC yields reported in this work range from 0.5–1.4% for carbon masses between 17 and 49 $\mu\mathrm{gC\,m^{-3}}$.

1 Introduction

Emissions of isoprene (C_5H_8) from vegetation constitute the greatest worldwide source of nonmethane hydrocarbons (Guenther et al., 1995). While it is well known that isoprene has a strong influence on levels of atmospheric gas-phase oxidants, it has only been determined recently that isoprene also plays a role in secondary organic aerosol (SOA) formation in the ambient atmosphere. Claeys et al. (2004a) deduced the presence of isoprene SOA by detecting two polyols, 2-methylthreitol and 2-methylerythritol, from filter samples of particulate matter taken in the Amazon rainforest. Following this report, the two methyl tetrols together with 2 methylglyceric acid (2-MGA) were found in a wide range of air environments including urban-impacted areas, semirural and forested areas, and remote areas (Ion et al., 2005; Edney et al., 2005; Kourtchev et al., 2005, 2008). Subsequently, the methyl tetrols were used as tracer compounds to estimate the contribution of SOA from isoprene in several different ambient areas worldwide (Kleindienst et al., 2007b; Lewandowski et al., 2008; Hu et al., 2008).

Secondary organic aerosol from the photooxidation of isoprene has also been examined in a limited number of laboratory studies in the presence and absence of oxides of nitrogen (NO_x). Most of the work has involved the use of smog cham-

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bers to study aerosol products generated under carefully controlled conditions. Edney et al. (2005) studied secondary organic carbon (SOC) products at NO_x levels of 600 ppb and found low SOC yields (ca. 0.001), although subsequent examinations found the yield to be highly dependent on the initial reactant concentrations. The addition of SO_2, known to photochemically generate acidic sulfate aerosol, led to a substantial increase in the SOC yield (Edney et al., 2005). In other studies, Kroll et al. (2005) and Dommen et al. (2006) conducted C_5H_8/NO_x irradiations and found aerosol yields ranging from 0.002–0.049. Kroll et al. (2006) also measured SOA by irradiating isoprene in the absence of NO_x using the photolysis of H_2O_2 to generate hydroxyl radicals (OH) directly. Aerosol yields in the range of 0.009–0.036 were found, although they reported a rapid loss of SOA during the irradiation. Kleindienst et al. (2007a) examined SOA formation from the C_5H_8+O_3 reaction and found a yield of 0.01 for an organic mass loading (M_0) of about 20 $\mu g\,m^{-3}$. Recently, Ng et al. (2008) measured SOA yields for C_5H_8+NO_3 reaction and reported values from 0.04–0.24.

These laboratory findings have been incorporated into atmospheric models to understand the contributions that isoprene oxidation might make to ambient organic carbon (OC) concentrations on global (Henze and Seinfeld, 2005) and regional scales (van Donkelaar et al., 2007; Lane and Pandis, 2007; Zhang et al., 2008). Results from the regional studies suggest that isoprene SOA products could account for an increase to $PM_{2.5}$ of 0.6 to as high as 3.8 $\mu g\,m^{-3}$ in the planetary boundary layer. Results from the global studies suggest an increased aerosol loading of up to a factor of three in the free troposphere. However, the results from these studies were highly sensitive to the selection of the enthalpy of vaporization for isoprene SOA. In addition, low molecular-weight carbonyl or dicarbonyl compounds (e.g. glyoxal, methylglyoxal, glycolaldehyde) thought to polymerize in a condensed phase, particularly during cloud formation, have also been suggested as possible isoprene secondary aerosol components (Matsunaga et al., 2005).

Measurements of 2-MGA, 2-methylthreitol, and 2-methylerythritol in ambient aerosol samples have provided the primary experimental basis for the presence of isoprene SOA in the atmosphere. (In the present paper, the three compounds when considered together will often be referred to as the isoprene SOA tracer compounds.) The vast majority of these measurements have involved filter collections followed by extraction and derivatization of the organic aerosol component with a trimethylsilylating (TMS) reagent. This approach does not measure 2-MGA and the methyl tetrols directly but only their TMS-derivatives. As a result, the exact form of the derivative precursors can be uncertain (Surratt et al., 2007; Sato, 2008). Notwithstanding these issues, it is likely that filter sampling followed by organic analysis and measurement of the TMS-derivatives will continue to represent a key experimental method for evaluating the contribution of isoprene SOA in the atmospheric aerosol.

Recently, Böge et al. (2006) examined the dark formation of the methyl tetrols in aerosol-phase from isoprene or specific photooxidation products in the presence of hydrogen peroxide (H_2O_2) and acidic sulfate seed aerosol. At an isoprene concentration of 1.5 ppm there was no evidence for 2-methyl tetrol formation, while at 5 ppm isoprene, 6 $ng\,m^{-3}$ of the 2-methyl tetrols were formed. By contrast, 1.5 ppm of the gas-phase products, 2-methyl-3-butene-1,2-diol (a product from C_5H_8+OH) and 2-methyl-2-vinyloxirine (a product from C_5H_8+O_3 or NO_3), when individually introduced into the chamber with H_2O_2 and acidic sulfate aerosol, resulted in substantially higher levels of 2-methylthreitol and 2-methylerythritol than that found in the isoprene system. These results appear to be consistent with the formation of the 2-methyl tetrols from liquid phase reactions in the isoprene-H_2O_2-sulfuric acid system (Claeys et al., 2004b). However, at present, it is unclear the degree to which the 2-methyl tetrols might form in the absence of acidic sulfate aerosol.

In this work, we have sought to clarify several of the issues which have arisen in the effort to understand the formation of SOA from isoprene, especially with respect to the formation of 2-MGA and the 2-methyl tetrols. In this work, emphasis is placed on studying SOA formation from the photooxidation of isoprene in the absence of NO_x, since isoprene aerosol does not appear to form until RO_2+HO_2 reactions become important (Dommen et al., 2006). As part of this effort, we have examined the relationship of the gas-phase intermediates to the isoprene tracer compounds formed during irradiation and whether acidic sulfate aerosol is essential for the formation of the 2-methyl tetrols. Several bulk properties, important in modeling isoprene SOA, have also been determined, including the effective enthalpy of vaporization (ΔH_{vap}^{eff}), the SOA-to-SOC ratio (SOA/SOC), and the aerosol yield. For the first two of these parameters, there is no experimental data available and isoprene SOA yields in the absence of NO_x have only been reported by Kroll et al. (2006). In addition, yields of the methyl tetrols and 2-MGA were measured to determine mass fractions of these isoprene tracer compounds similar to the method of Kleindienst et al. (2007b). While the focus of this work is on a study of SOA in the absence of NO_x, a limited number of irradiations were conducted to generate SOA from the isoprene/CH_3ONO/NO_x system primarily to obtain experimental data for ΔH_{vap}^{eff} and OM/OC, which presently are not available.

2 Experimental methods

Many aspects of the experimental system have been previously described (Kleindienst et al., 2006). The reaction chamber is a 14.5-m^3 parallelepiped, stainless-steel chamber with interior walls fused with a 40 μm TFE Teflon coating. The chamber uses a combination of fluorescent bulbs that provide radiation distributed over the portion of the spectrum from 300-400 nm similar to solar radiation. For experiments requiring the photolysis of H_2O_2, UV-sunlamps (UV-313) were added to the irradiation system to increase the intensity of the radiation from 280–320 nm, since without these bulbs H_2O_2 would not photolyze significantly. (However, the use of these lights could also increase the photolysis rate of organic peroxides formed from the photooxidation.) The smog chamber was operated as a continuous stirred tank reactor with a total flow of $47\,\mathrm{L\,min^{-1}}$ to produce a steady-state gas mixture. Reactants were added to the chamber continuously with the effluent being withdrawn at the same flow rate for filter collection and on-line gas and particle analysis.

During the irradiation, reactants were added to the chamber by several different means. Where possible, dilute mixtures in high pressure cylinders were used, for isoprene, methyl nitrite (CH_3ONO), and nitric oxide (NO). Hydrogen peroxide (50% aqueous mixture, Aldrich Chemical Co.) was injected by a syringe pump into a heated glass bulb where it vaporized and then was mixed rapidly in the chamber through the dilution air flow. Typical H_2O_2 liquid flow rates ranged from 0.09 to $0.27\,\mathrm{mL\,h^{-1}}$. H_2O_2 concentrations were estimated by UV absorption by drawing the reactant mixture through a conventional ozone monitor. At 254 nm, the ozone extinction coefficient is a factor of 141 times greater than that of H_2O_2. The ozone monitor provides an estimate of the gas-phase H_2O_2, because the ozone scrubber in the monitor is expected to be highly efficient at removing H_2O_2 from the air stream; thus, H_2O_2 is measured as though it were ozone but with a substantially reduced extinction coefficient. Except for a negligible amount of water introduced with H_2O_2, these experiments were conducted dry. (However, one experiment using CH_3ONO/NO as the oxidant mixture used a relative humidity of 30%.) The experiments were conducted dry to minimize the uptake of H_2O_2 onto an aqueous aerosol that could be present at relative humidities above the relative humidity of efflorescence of ammonium sulfate, ca. 35%. To aid aerosol formation, ammonium sulfate seed aerosol at less than $1\,\mu\mathrm{g\,m^{-3}}$ (volume modal diameter of 80 nm) was added to the chamber by nebulizing a $10\,\mathrm{mg\,L^{-1}}$ ammonium sulfate solution. The average chamber temperature was 24.2°C and the average residence time of the gases in the chamber was 5.1 h during the steady-state experiments.

Selected chemical and physical parameters were monitored continuously during the flow-mode experiments. For a subset of experiments, NO and total NO_y were measured with a ThermoElectron (Model 8840, Thermo Environmental, Inc., Franklin, MA) oxides of nitrogen chemiluminescence analyzer. Isoprene levels in the chamber and inlet manifold were measured by gas chromatography (Model 5890, Hewlett Packard, Palo Alto, CA). Measurements were also made by GC for methacrolein and methyl vinyl ketone (MVK), two of the major carbonyl compounds produced during isoprene photooxidation. Concentrations were determined using an effective carbon number of 0.8 for C_4-carbonyl compounds (Scanlon and Willis, 1985). Temperature and relative humidity were measured with an Omega Digital Thermo-Hydrometer (Model RH411, Omega Engineering, Inc., Stamford, CT).

The number, surface, and volume distributions of the aerosol were measured using a scanning mobility particle sizer (SMPS; TSI, Inc., Shoreham, MN). In this study, this information was generally used for diagnostic purposes only, although from the volume measurements, the volatility of the photochemically-produced organic aerosol could be determined using the Volatility Differential Mobility Analysis (VDMA) technique (Offenberg et al., 2006). The technique requires only the relative change in volume. The use of $\Delta H_{\mathrm{vap}}^{\mathrm{eff}}$ in this context is simply as an operational parameter to represent the change in the volatility of composite aerosol as a function of temperature. Unlike techniques which use tandem DMAs (e.g. Paulsen et al., 2006), this method uses a 25-cm heated line coupled to the inlet to measure the integrated volume over the entire SMPS size range (18–931 nm). The technique is feasible because in the steady-state mode the chamber aerosol volume remains constant over the course of the measurements. At each stage of the analysis, the volume distribution of the aerosol is allowed to equilibrate at preset temperatures between room temperature and 250°C. For this study, volume measurements were generally taken for analysis at 50, 100, 150, 200, and 250°C. The natural logarithm of the integrated aerosol volume measured experimentally is found to correlate linearly with the inverse of the temperature. From the slope of this relationship (ln V vs. T^{-1}), $\Delta H_{\mathrm{vap}}^{\mathrm{eff}}$ is directly determined for the aerosol (Offenberg et al., 2006).

The organic carbon concentrations formed during the irradiations were measured using an automated, semicontinuous elemental carbon (EC)-OC instrument developed by Sunset Laboratories (Tigard, OR). Since elemental carbon was not present in these systems, the measured total carbon was equivalent to SOC. The instrument operated at a flow rate of $8\,\mathrm{L\,min^{-1}}$ with a sample collection time of 30 min. Using a thermooptical analytical technique (Birch and Cary, 1996), the total time for analysis was 12.5 min. Given a reequilibration time of 2.5 min, the instrument operated on a 45-min duty cycle. In addition to SOC, the organic mass (OM; equivalent to SOA in this work) concentration of the same steady-state air mass was determined by gravimetric analysis of an integrated aerosol sample collected onto a 47-mm Teflon-impregnated glass fiber filter at a flow rate of $16.7\,\mathrm{L\,min^{-1}}$. OM values were typically collected over 4– 20 h periods. For measurements of OM/OC (i.e. SOA/SOC), SOC values were determined as the average of the semicontinuous OC measurements over the same period as the filter collection for the gravimetric determination.

Organic peroxides in SOA were determined in a manner similar to that of Docherty et al. (2005). The technique assumes that the organic peroxides formed in the isoprene system have a molar absorption coefficient that can be ad-

Table 1. Initial conditions for the formation of secondary organic aerosol from the photooxidation of isoprene in the absence and presence of NO_x. CH_3ONO and H_2O_2 served as the OH precursors in experiments with and without NO_x, respectively.

Experiment	Isoprene (ppmC)	H_2O_2 , $CH_3ONO^{\dagger}$ (ppm)	NO, (ppm)	Temperature (C)	RH (%)
1a, b	12.0	4.9	0.0	24.8	<3
2	15.7	7.3	0.0	24.5	<3
3	7.67	2.7	0.0	24.5	<3
4	15.5	2.7	0.0	24.5	<3
5a, b	15.4	12.9	0.0	24.4	<3
6	8.10	$0.20^{\dagger}$	0.23	22.8	30.5
7*	8.10	$0.20^{\dagger}$	0.23	22.8	30.5
8	10.9	$0.24^{\dagger}$	0.19	24.4	<3

* Experiments conducted consecutively as a single run with the light intensity of Experiment 7 one-half of that in Experiment 6.

† Initial methyl nitrite concentration.

equately represented by the calibration compound, benzoyl peroxide (MW 242 g mol^{-1}), one of the few organic peroxides available commercially. Aerosol from the chamber was collected onto glass-fiber filters during short (2–4 h) or long term (24 h) sampling periods. After collection, laboratory and blank filters were immediately extracted by sonication for 1 h in 10 mL vials containing 8 mL ethyl acetate. Following extraction, 2 mL of each extract was added to 3 mL of an acetic acid-chloroform-water solution (0.53:0.27:0.20 by volume) in 10 mL airtight vials. Each solution was then sparged for 10 min with N_2 to remove O_2. After the purging period but with N_2 still flowing through the headspace of the solution, 50 mg of potassium iodide was added to the solution. After shaking, the solution was allowed to react for 2 h with N_2 still flowing. At the same time, calibration solutions of benzoyl peroxide were treated in a manner identical to the sample and blank. The solution absorbance at a wavelength of 470 nm was then measured using a Spectronic 20 D+ spectrophotometer (Thermo Electron Corp., Austin, TX) relative to the solution blank using matched 10-mm quartz cells. The molar concentration of total peroxide was calculated from the absorbance using a standard calibration curve prepared from the series of benzoyl peroxide solutions.

Individual organic compounds in the gas and particle phase were determined using gas chromatography-mass spectroscopy (GC-MS) analysis of filter samples. The sampling train consisted of an organic denuder to remove gas-phase organic compounds followed by 47-mm Teflon-impregnanted glass-fiber filters for aerosol-phase compounds. The extractable denuder developed at the Lawrence Berkeley National Laboratory (Gundel et al., 1995) contains eight concentric glass tubes (University Research Glass, Chapel Hill, NC) coated with the XAD-4 solid phase adsorbent. The coating was chemically-bonded to the glass denuder using a proprietary technique developed by Restek Corporation (Bellefonte, PA). The 60-cm, 8-channel denuder has an internal volume of approximately 500 cm^3 giving an effluent residence time of 2 s in the denuder. Further details regarding the denuder operation are given by Kleindienst et al. (2004).

Filter samples were Soxhlet extracted for 6 h using a dichloromethane/methanol mixture (80:20) to which 20 μg of *cis*-ketopinic acid was added as an internal standard. Samples were extracted from the denuder using a 25:25:50 hexane/methylene chloride/acetonitrile mixture. The denuder and filter extracts were dried and derivatized with 250 μL bis (trimethylsilyl)-trifluoroacedimide (BSTFA) and 100 μL of pyridine. GC-MS analysis was conducted with a ThermoQuest (GCQ-Plus; Austin, TX) GC coupled to an ion-trap MS operated in a chemical ionization (CI) mode. Two microliters of the extract were injected into the GC operated in a splitless mode. Compounds were separated on a 60-m-long, 0.25-mm-i.d. RTx-5MS capillary column (Restek, Inc., Bellefonte, PA) with a 0.25-μm film thickness with other chromatographic conditions as previously described (Jaoui et al., 2004).

The initial conditions for the eight experiments in this study are given in Table 1. The first five experiments were conducted in the absence of NO_x and the last three with CH_3ONO and NO present. Initial isoprene concentrations ranged between 1.5–3.1 ppm, H_2O_2 between 2.7–12.9 ppm, CH_3ONO between 0.20–0.24 ppm, and NO between 0.19–0.23 ppm. Some of the experiments (as noted below and in the tables) were conducted in multiple parts. Each part (listed as a or b) of a numbered experiment was conducted at the same initial conditions given by the table. This was mostly done to permit additional samples to be taken for analyses requiring, for example, different collection masses or sampling times. As a result, not all parameters were measured during each experiment or part of an experiment which is readily seen in the tables of results. Experiments were performed in a steady-state mode and a gas mixture was given three residence times to achieve the new steady-state level before sampling started.

Table 2. Steady-state chamber and reacted hydrocarbon concentrations for flow-mode experiments.

Experiment	NO_y (ppm)	O_3 (ppm)	Isoprene (ppmC)	Δ Isoprene (ppmC)	Methacrolein (ppm)	MVK (ppm)
1a, b	0.0	0.0	4.77	7.23	–	–
2	0.0	0.0	9.30	6.42	–	–
3	0.0	0.0	5.46	2.21	0.041	0.066
4	0.0	0.0	8.37	7.11	0.15	0.26
5a, b	0.0	0.0	7.75	7.68	0.17	0.30
6	0.296	0.353	0.16	7.94	–	–
7	0.181	0.186	2.00	6.10	–	–
8	0.372	0.270	1.80	9.12	0.27	0.22

3 Results

Steady-state chamber concentrations of isoprene, NO_y, and O_3, where applicable, are given in Table 2. For experiments without NO_x, the photolysis of H_2O_2 was the only source of OH, since OH cannot be generated by catalytic means in these types of photochemical systems without involving NO_x. The reacted isoprene is also shown in Table 2 and calculated from the difference of the initial and steady-state isoprene concentrations. In all cases, the initial isoprene concentration was determined from the measured isoprene concentration in the inlet manifold scaled by a measured dilution factor. For Experiments 1–5, the range of reacted isoprene concentrations was 2.2–7.7 ppmC. The random uncertainty in the reacted isoprene is determined from the reproducibility of both the initial and steady-state isoprene values by gas chromatography and generally ranges from 20–30%.

Also shown in Table 2 are steady-state chamber concentrations for three runs with NO_x present in the reactant mixture. In each case, the photolysis of CH_3ONO was used to generate OH initially. With the chamber at steady state, CH_3ONO and NO had reacted completely while the fraction of reacted isoprene was in the range 0.61–0.98. Substantial concentrations of NO_x and ozone were present at steady state as seen in Table 2, Experiments 6–8. Given the low steady-state concentrations of NO, it is likely that peroxy-peroxy radical (RO_2–RO_2) reactions were occurring, at least to a modest extent, in the systems with NO_x.

For Experiments 3, 4, 5, and 8, measurements were also made of the major C_4-carbonyl products formed during the photooxidation of isoprene, methacrolein and methyl vinyl ketone (MVK). Measured steady-state concentrations are given in Table 2. For experiments without NO_x, the data consistently show MVK levels a factor of 1.7 higher than methacrolein. Yields for the formation of these compounds as the major carbonyl products have already been described for the photooxidation of isoprene in the presence of NO_x (Carter and Atkinson, 1996; Fan and Zhang, 2004) and in its absence (Jenkin et al., 1998). Since the two products are reported to form with nearly equal yields (Jenkin et al., 1998), secondary reactions of methacrolein could be more rapid than those from MVK in this system given the much higher concentrations detected for MVK in the absence of NO_x. Methacrolein is the presumed precursor to the aerosol product, 2-MGA (Szmigielski et al., 2006).

With the chamber operated in a steady-state mode, a constant aerosol source was maintained for each initial condition given in Table 1. The major aerosol parameters measured, SOA and SOC, are given in Table 3. Uncertainties in the SOC values are taken from the reproducibility of the semi-continuous measurement and are typically better than 10% for a single run. For OM, the uncertainties are determined from the reproducibility of side-by-side filter measurements which are typically better than 5%. An estimate of the systematic errors due to minor changes in reactant concentrations, minor variations in chamber temperature, and other similar factors bring the total uncertainty to between 15 and 25% for these parameters. SOA/SOC values were then determined from the corrected data and given in Table 4. For experiments in the absence of NO_x, SOA/SOC values ranged between 1.77 and 2.04 with an average value of 1.9. Similarly in the presence of NO_x, the measured values were between 1.46 and 1.52 with an average value of 1.5.

From the organic aerosol produced in the isoprene photooxidation in the absence and presence of NO_x, an effective enthalpy of vaporization was determined using the VDMA. Figure 1 shows the change in the integrated volume of the steady-state aerosol subjected to five temperatures as measured in Experiment 3. For each temperature, five to seven measurements of the particle volume were made. Error bars in the plot represent the reproducibility of the integrated volumes from 5–7 measurements. The plot of ln V vs. T^{-1} shows a linear relationship with a slope of – 4894 K^{-1}, when multiplied by the Gas Constant, R, gives a ΔH_{vap}^{eff} of 40.7 kJ mol^{-1}. Values of ΔH_{vap}^{eff} for the other experiments in which the measurement was made are summarized in Table 4. For the experiments without NO_x present, ΔH_{vap}^{eff} ranges between 34 and 41 kJ mol^{-1} with an average value 38.4 kJ mol^{-1}. For the two experiments with NO_x where ΔH_{vap}^{eff} was measure, an average value of 43.2 kJ mol^{-1} was determined.

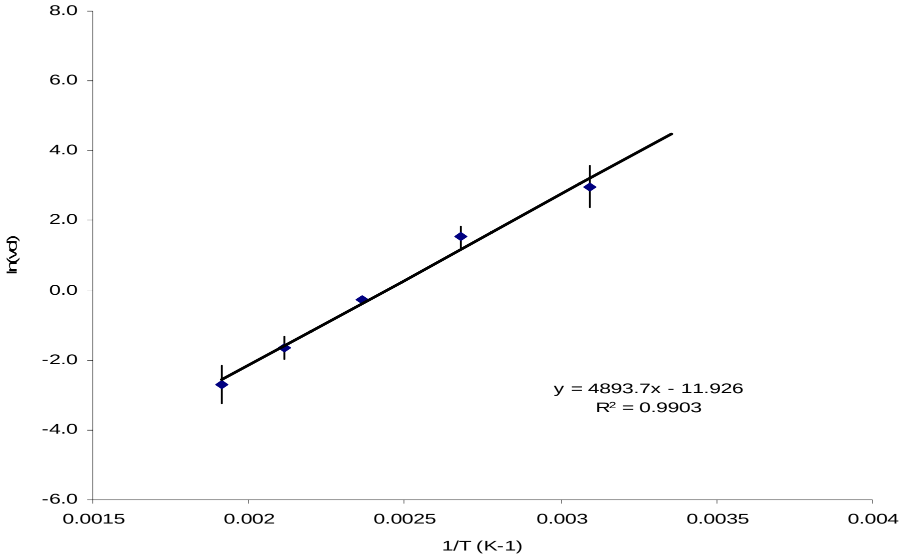


Fig. 1. Measured ΔH_{vap}^{eff} of organic aerosol generated from the isoprene + OH reaction conducted in the absence of NO_x in Experiment 3.

Table 3. Formation and yields of SOA (Y_{SOA}) and SOC (Y_{SOC}). All organic and carbon aerosol masses are corrected for a wall loss of $0.067\,h^{-1}$. A carbon mass for isoprene of $60.06\,g\,mol^{-1}$ is used for the SOC yield calculation.

Experiment	Reacted Isoprene ($mg\,m^{-3}$)	SOA ($\mu g\,m^{-3}$)	SOC ($\mu gC\,m^{-3}$)	Y_{SOA} (%)	Y_{SOC} (%)
1a	4.03	76.5	38.6	1.90	1.09
1b	4.03	79.3	49.4	1.97	1.39
2	3.58	73.0	35.8	2.04	1.13
4	3.96	30.7	16.6	0.78	0.48
5a	4.28	49.6	26.2	1.16	0.69
6	4.42	69.2	47.2	1.57	1.22
7	3.40	11.6	–	0.39	–
8	5.09	83.5	54.8	1.64	1.22

Organic carbon and organic aerosol yields were determined for each experiment except for Experiment 3. The secondary organic carbon yield (Y_{SOC}) and the secondary organic aerosol yield (Y_{SOA}) were calculated from the following respective relationships:

$$Y_{SOC}=SOC/\Delta HC_C \tag{1}$$

$$Y_{SOA}=SOA/\Delta HC \tag{2}$$

where SOC is the organic carbon concentration and ΔHC_C is the reacted isoprene carbon concentration found in Table 2. In Eq. (2), SOA is the corrected organic aerosol mass concentration and ΔHC is the reacted isoprene mass concentration. SOA and SOC were also corrected for wall loss to the chamber which had previously been determined for organic aerosol to be $0.067\,h^{-1}$. Uncertainties in the yield come from the experimental uncertainties in SOA, SOC, and the reacted isoprene concentrations, as discussed earlier.

Yields for the experiments conducted in the absence of NO_x are found in Table 3. Experiment 1 was conducted in two parts and showed the reproducibility of Y_{SOA} and Y_{SOC} to be approximately 4% and 20% respectively. Y_{SOA} values were determined for SOA concentrations from 30–80 $\mu g\,m^{-3}$ and ranged between 0.8 and 2.0%; similarly, Y_{SOC} was measured for SOC concentrations from 17–50 $\mu gC\,m^{-3}$ and found to range between 0.5 and 1.4%. Selected yields in the presence of NO_x are also given for Experiments 6–8. For the two systems at similar SOA concentrations, the yields tended to be higher for experiments without NO_x. This may also be due to the fact that the reaction of isoprene with NO_x tends to generate carbonyl products which may not lead to SOC formation over the time scale of these experiments. However, for cases both in the absence or presence of NO_x, the data in Table 3 indicate that Y_{SOA} and Y_{SOC} were lower at the lower SOA and SOC concentrations, respectively.

Table 4. Experimental values for the organic mass to organic carbon ratio (OM/OC), the effective enthalpy of vaporization (ΔH_{vap}^{eff}) and the total organic peroxide mass determined in the study. (Organic peroxide molar values converted to mass values assuming a molecular weight of 150 g mol^{-1}.)

Experiment	OM/OC	ΔH_{vap}^{eff}	Organic Peroxide (μg m^{-3})	Organic Peroxide (%)
1	1.77[a]	40.0	–[b]	–
2	2.04	–	–	–
3	–	40.7	–	–
4	1.85	–	7.41	24.1
5[c]	1.88	34.5	11.6	23.4
6	1.46	42.0	–	–
8	1.52	44.4	–	–

[a] average from Experiment 1a and b.

[b] not determined/sample not taken.

[c] includes data from both experimental parts a and b.

Formation of organic peroxides was readily evident in the experiments in the absence of NO_x. As noted, the experiments were conducted under dry conditions to preclude the possibility that H_2O_2 might be taken up into an aqueous aerosol phase. Organic peroxide measurements were made only during Experiments 4 and 5 as shown in Table 4. Since the analytical technique only gives a molar value, an average molecular weight 150 g mol^{-1} was assumed in order to determine the mass concentrations of organic peroxides for comparison with the total SOA mass. In each experiment, approximately one-quarter of the aerosol was measured as organic peroxides given the assumptions adopted.

The isoprene SOA tracer compounds have previously been reported in laboratory irradiations of isoprene (Edney et al., 2005) and from field samples, particularly in areas having strong isoprene emissions (Claeys et al., 2004a). While low levels of SOA were detected from isoprene/NO_x irradiations, the tracers were found to increase dramatically along with an increased formation of SOA following the addition of SO_2 with the likely formation of acidic sulfate aerosol in the system (Edney et al., 2005; Surratt et al., 2007; Jaoui et al., 2008). In this work, an examination of the gas phase has also been conducted to evaluate the possible formation of intermediates in the absence of NO_x which may be relevant in producing the 2-methyl tetrol tracer compounds.

The TMS-derivatized denuder extract showed the presence of four peaks consistent with the presence of four methyl butenediol isomers as shown in Figure 2a. There was no evidence for these compounds in the blank sample. The methyl butenediols have a molecular weight (M_C) of 102 Da with a derivative molecular weight (M_d) of 246 Da. Two of the compounds, 2-methyl-3-butene-1,2-diol and 3-methyl-3-butene-1,2-diol, have already been reported (Ruppert and Becker, 2000) and the other two compounds are possibly E- and T-2-methyl-2-butene-1,4-diol. These compounds, as represented by their base ion m/z 231 in Fig. 2a, elute at retention times prior to 2-MGA (see below). For the particle phase sample, this chromatographic region (scaled to the same degree as the gas phase) shows minor levels of the methyl butenediols (<5%). The mass spectra of the four isomers are extremely similar and a representative mass spectrum is given in Fig. 2c. As in many TMS derivatives detected by CI, the M+1 ion (m/z 247) is typically very weak with the base peak being given by the M-15 ion fragment (i.e. m/z 231; loss of a methyl group). Also evident in the chromatogram is the M-89 peak (m/z 157; loss of an O-Si-$(CH_3)_3$ moiety) and the characteristic ions of TMS-compounds m/z 73, 147, and 149. Of particular interest is the presence of a weak M-1 fragment at m/z 245 in Peaks 2–4 of somewhat greater intensity than m/z 247. Wang et al. (2005) used a similar weak M-1 fragment to help justify the presence of a series of C_5-alkene triols found in field samples. This observation could well be applicable for the methyl butenediols.

There was some evidence that methyl tetrols might also be present at low levels in the denuder sample represented by Fig. 2. The finding could be attributed to the presence of the methyl tetrols in the gas phase based on estimated saturation vapor pressures for tetrols reported by Angove et al. (2006). However, it is also possible that, given the sampling flows used, a small amount of the aerosol, especially at small aerosol diameters, diffused to the denuder surface. In addition, a low level of the methyl tetrols was occasionally detected in the blank due to carryover.

From the particle phase extracts for Experiment 4, the SOA tracer compounds are clearly detected (Peaks 1, 6, and 7) in the isoprene photooxidation system in the absence of SO_2, NO_x, or acidic aerosol, as seen in the chromatogram in Fig. 3. The mass spectra for these TMS-derivatives are consistent with the mass spectra of the isoprene SOA tracer

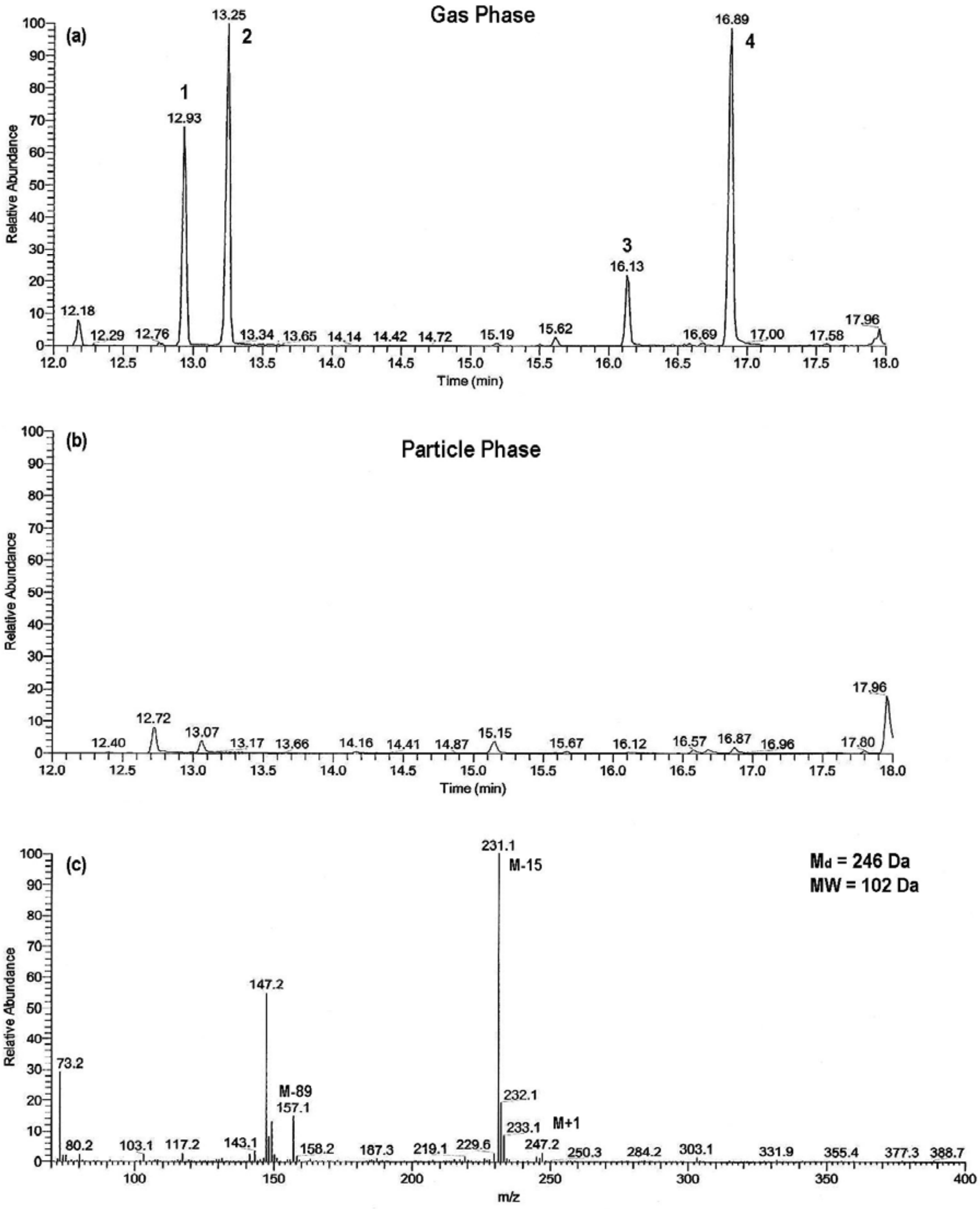


Fig. 2. Gas **(a)** and particle **(b)** phase chromatograms and mass spectrum **(c)**; (Peak 1) of the butenediols in Experiment 2. For clarity in (a) and (b), the selected ion m/z 231 is shown.

compounds which have already been published (Claeys et al., 2004a; Edney et al., 2005; Szmigielski et al., 2006).

Also detected chromatographically, as seen in Fig. 3, are a series of three C_5 alkene triol isomers (Peaks 2, 3, 4). They have been identified as *cis*-2-methyl-1,3,4-trihydroxy-1-butene; 3-methyl-2,3,4-trihydroxy-1-butene; and *trans*-2-methyl-1,3,4-trihydroxy-1-butene, and were also found in field samples and inferred as being formed during the photooxidation of isoprene (Wang et al., 2005; Kourtchev et al., 2005). The CI-mass spectrum for the three alkene triols are highly consistent with those already published by Wang et al. (2005). Under the experimental

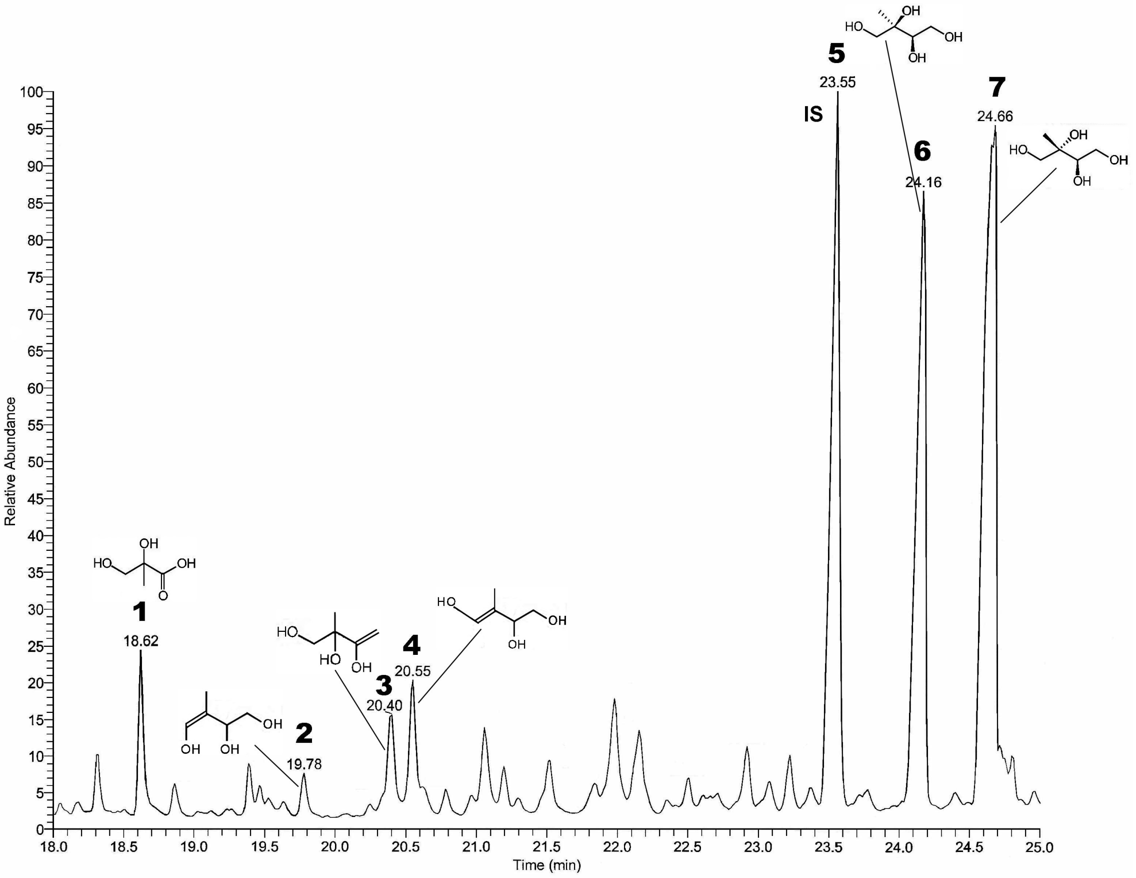


Fig. 3. Total ion chromatogram of filter extract of isoprene SOA formed in the absence of NO_x from Experiment 4. Identifications: **(1)** 2-methylglyceric acid; **(2)** *cis*-2-methyl-1,3,4-trihydroxy-1-butene; **(3)** 3-methyl-2,3,4-trihydroxy-1-butene; **(4)** *trans*-2-methyl-1,3,4-trihydroxy-1-butene; **(5)** Internal standard (*cis*-ketopinic acid); **(6)** 2-methylthreitol; **(7)** 2-methylerythritol.

conditions reported herein, the sum of the alkene triols is approximately 20% of that of the 2-methyl tetrols. While the triols were detected in all experiments in the absence of NO_x, in the other experiments, the sum of the alkene triols were generally less than one-tenth of the sum of the 2-methyl tetrols.

The concentrations of the 2-MGA, and the two 2-methyl tetrols were quantified as *cis*-ketopinic acid (KPA), since pure standards of the three compounds were not available. Given the magnitude of the isoprene SOA tracer compound peaks above the background and the purity of the peaks, a calibration factor based on the total ion chromatogram for KPA was used. An evaluation of the method (Jaoui et al., 2005) showed that the uncertainty introduced for the absolute concentrations using this approach was approximately 60% for the four biogenic tracers tested. Moreover, when KPA is used for both laboratory and field samples, systematic errors in absolute concentrations using the approach are offset provided the precursors and products are the same.

Table 5 gives concentrations for 2-MGA, 2-methyltheitol, and 2-methylerythritol formed in the experiments in the absence of NO_x. (Only in the experiments reported in Table 5 was sufficient aerosol mass collected to perform GC-MS analysis on the derivatized extracts.) As seen in Table 5, concentrations of 2-MGA ranged between 0.12 and 4.1 $\mu g\,m^{-3}$, for 2-methylthreitol between 0.7 and 11.4 $\mu g\,m^{-3}$, and for 2-methylerythritol between 1.1 and 15.1 $\mu g\,m^{-3}$. The tracer masses were then used together with the measured SOA or SOC masses to obtain tracer mass fractions useful for determining the contribution of SOA or SOC from isoprene in field samples (Kleindienst et al., 2007b; Lewandowski et al., 2008). The aerosol mass fraction, f_{SOA}, is determined as the fraction of the sum of the three isoprene tracer compounds to the SOA mass. Analogously, the aerosol carbon mass fraction for isoprene, f_{SOC}, is the fraction of the sum of the OC tracer compounds to the measured organic carbon (Kleindienst et al., 2007b). From the four experiments without NO_x present, f_{SOA} ranges from 0.06 to 0.12 and f_{SOC} from 0.12 to 0.23.

Table 5. Methyl tetrols and 2-MGA formed from irradiations in the absence of NO_x. Mass fractions of these tracer compounds (defined in text) to the organic mass (f_{SOA}) and organic carbon (f_{SOC}) are also given.

Experiment	2-MGA ($\mu g\,m^{-3}$)	2-Methylthreitol ($\mu g\,m^{-3}$)	2-Methylerythritol ($\mu g\,m^{-3}$)	f SOC	f SOA
1b	0.33	1.36	2.34	0.071	0.127
2	0.18	0.99	1.69	0.057	0.117
4	0.12	0.71	1.11	0.080	0.147
5b	4.1	11.4	15.1	0.123	0.231

4 Discussion

SOA formed during the reaction of isoprene + OH in the absence of NO_x shows the presence of the three isoprene tracer compounds, 2-MGA, 2-methylthreitol, and 2-methylerythritol. While these findings are consistent with those of Edney et al. (2005), the yields of SOA and isoprene tracers are considerably greater than those reported where NO_x is present (in the absence of SO_2). Böge et al. (2006) also reported detecting the 2-methyl tetrols in dark experiments using the presumed gas-phase products of the isoprene photooxidation system. However, Böge et al. (2006) found that the 2-methyl tetrols formed only in the presence of acidic sulfate aerosol. Thus, in that work isoprene sulfates might have been formed as described by Surratt et al. (2007). In the present experiments, the isoprene tracer compounds are readily formed in the absence of acidic sulfate with only neutral sulfate seed aerosol being present. As noted earlier, H_2O_2 is most likely to have remained completely in the gas-phase during the irradiations given the dry conditions for the present experiments. Thus, a gas-phase mechanism is possible and one such possibility is considered in Scheme 1.

The identification of stable gas-phase intermediates may provide some insight into methyl tetrols formed during the photooxidation of isoprene. The formation of the 2-methyl butenediols in the gas phase has already been reported by Ruppert and Becker (2000). This type of reaction has long been recognized from the disproportionation reaction of RO_2 radicals in the liquid phase (Russell, 1957). Barnes et al. (1993) determined that a disproportionation reaction must be occurring in the gas-phase reaction of ethylene with OH in the absence of NO_x, from the observation of a C_2-diol and glycolaldehyde. While this same reasoning was used for isoprene, OH can initially add to four possible isoprene positions, resulting in eight possible intermediate radicals that can be formed following the addition of O_2 to the initial hydroxylated radical (Ruppert and Becker, 2000). The diol can then be formed following a disproportionation reaction involving two RO_2 radicals to produce an alcohol (in this case a diol) and an aldehyde, as depicted in the first two reactions of Scheme 1. While Ruppert and Becker (2000) detected the presence of two isomers (2- and 3-methyl-3-butene-1,2-diol) from the 1,2-OH addition, two other isomers from the 1, 4-addition (E- and T-2-methyl-2-butene-1,4 diol) though predicted were not detected. In the present work, four peaks having derivative molecular weights of 246 (Fig. 2) have been tentatively identified as the four possible butenediol isomers. Presently, it is not possible to assign specific compound structures to the peaks given the minor differences in the mass spectra. However, the observation of two additional butenediol compounds detected in this work not seen by Ruppert and Becker (2000) might be explained by differences in the chamber surface-to-volume ratios, irradiation systems, reaction times, or the initial conditions for the reactive systems.

The formation of the methyl butenediols through the RO_2 disproportionation reaction might be expected to compete poorly with the formation of organic hydroperoxides given the greater propensity of RO_2 to react with HO_2 rather than with a second RO_2 radical under low NO_x conditions (Lightfoot et al., 1992). In fact, the rate constant for a typical RO_2+RO_2 reaction is approximately an order of magnitude lower than the RO_2+HO_2 rate constant for primary peroxy radicals and an additional order of magnitude lower for secondary or tertiary peroxy radicals, although the presence of a β-hydroxy peroxy radical can increase the RO_2+RO_2 rate constant (Jenkin and Hayman, 1995). Nevertheless, with the relatively low H_2O_2-to-isoprene ratios being used, the $OH+H_2O_2 \rightarrow HO_2+H_2O$ reaction does not compete effectively with the isoprene + OH reaction, resulting in a system poor in HO_2. The major source of HO_2 in this system comes from reactions of RO radicals either through abstraction by O_2 or their decomposition or isomerization, where the RO radicals can only be formed from RO_2+RO_2. Thus, under conditions where there are no other sources of HO_2 (e.g. the conditions of Ruppert and Becker, 2000, and experiments herein), HO_2 production is limited by the RO_2+RO_2 reaction itself. Once HO_2 is formed, it reacts rapidly with RO_2 to produce a C_5-hydroxy-hydroperoxide (Reaction 3), which can then undergo further reactions. Ruppert and Becker (2000) have shown through a mass balance approach that RO_2+RO_2 reactions produces stable products (diols and hydroxycarbonyls) 25% of the time and radical products (RO) the other 75%. Furthermore, assuming no sources of HO_2 other than from reactions of RO, the system still produces a hydroperoxide-to-diol ratio of six. (This ratio would be considerably higher if other sources of HO_2 were available.) The conditions of Ruppert and Becker (2000) are expected to apply in these experiments.

Since hydrogen peroxide is an interference with the organic peroxide technique described above, it was not possible to measure the total organic peroxide in the gas phase. As an alternative, the chromatogram from the denuder sample was examined for an aldehydic co-product formed with the butenediols that might be detected in the gas phase. Such a product would be a hydroxy carbonyl having a molecular weight of 100 Da and a derivative molecular weight of 244 Da. While there is some evidence for such a compound, the ion intensities of the mass spectra are far too low to justify its importance as a co product of a butenediol. However, this was not completely unexpected given that Ruppert and Becker (2000), while finding FTIR evidence for the presence of organic hydroperoxides in the gas phase, also did not detect the presence of aldehydic co-products for the butenediols. Thus, these compounds may have been removed from the system by a rapid secondary reaction or have photolyzed.

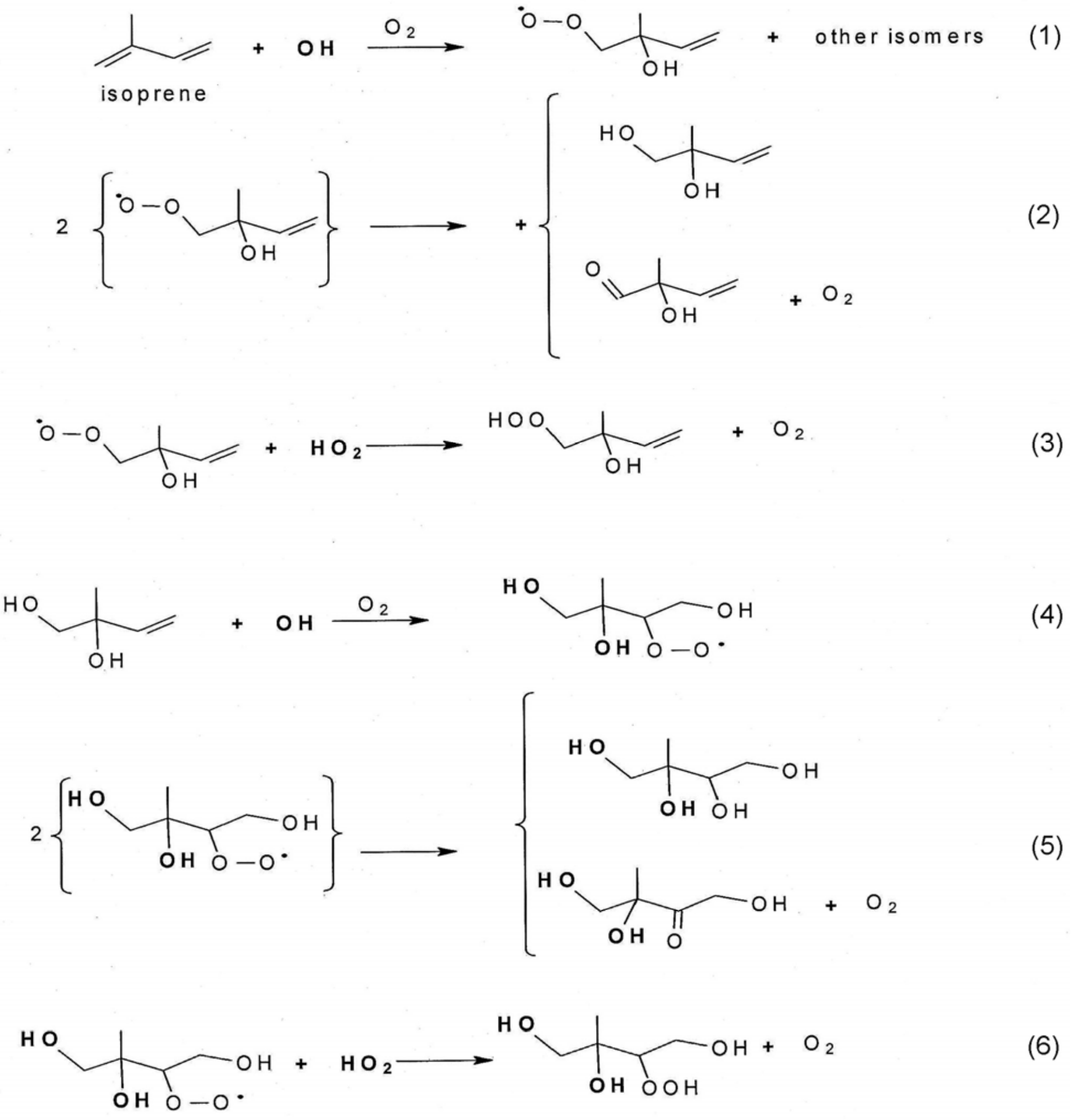
In the particle phase, numerous polyols were detected in the laboratory samples. We first consider the three alkene triols detected. The alkene triols have previously been observed in field samples in areas highly impacted by vegetative emissions (Wang et al., 2005; Kourtchev et al., 2005). These compounds have molecular weights of 118 Da, derivative molecular weights (M_d) of 334 Da, and elute at retention times between 2-MGA and 2-methylthreitol. Given the similarities in chromatographic systems, the compound assignments of Wang et al. (2005) are likely to hold in this study, that is, *cis*-2-methyl-1,3,4-trihydroxy-1-butene; 3-methyl-2,3,4-trihydroxy-1-butene; and *trans*-2-methyl-1,3,4-trihydroxy-1-butene, respectively, for peaks 2, 3, and 4 in Fig. 3. The initial report of their detection (Wang et al., 2005) suggested that the compounds formed from an acid catalyzed decomposition of a C_5-epoxide. Under the experimental conditions of this study where SOA condensed onto neutral ammonium sulfate seed aerosol, the hypothesis of Wang et al. (2005) regarding epoxide decomposition in the aerosol could not be confirmed and suggest alternate pathways for forming the alkene triols might be present.

Kourtchev et al. (2005) also detected the alkene triols under summer conditions within a boreal forest and found that the sum of the alkene triols was, in some cases, as great, if not greater than the 2-methyl tetrols. As noted earlier, in no cases during these experiments were the alkene triols more than 20% of the 2-methyl tetrols and in most cases less than 10%. If the alkene triols were to be precursors to the methyl tetrols, this finding would suggests that the oxidation of isoprene in their field samples might have been less advanced than that observed in the laboratory, i.e. in the laboratory the losses of the alkene triols might be accentuated, possibly because of the high OH levels in the system.

The reaction of isoprene + OH in the absence of NO_x produces methacrolein at high yields in the gas phase. Methacrolein subsequently undergoes further oxidation to produce methylglyceric acid which partitions into the particle phase where it is detected (Szmigielski et al., 2006). Turning to the 2-methyl tetrols, one possible mechanism for generating them could be via a second disproportionation channel similar to that described for the 2-methyl butenediols. This formation pathway to produce the methyl tetrols from the dihydroxy-RO_2 radicals is shown by Reactions 4–5. Again while the reaction of RO_2+HO_2 generally dominates the RO_2+RO_2 reaction, the presence of a β-hydroxy peroxy radical (in this case having multiple OH groups) can increase the rate constant for the self reaction by one to two orders of magnitude (Jenkin and Hayman, 1995). However, as noted earlier, the rate constant for the RO_2+RO_2 reaction decreases substantially for secondary and tertiary peroxy radicals (Jenkin and Hayman, 1995). Taken together these factors suggest that the RO_2+RO_2 rate constants could be approximately an order of magnitude slower than the RO_2+HO_2 rate constants. The limitation of HO_2 radicals, since they formed from slow RO radical reactions, again mitigates the importance of the RO_2+HO_2 channel.

The disproportionation reactions to form the 2-methyl tetrols are analogous to reactions proposed by Angove et al. (2006) to explain the formation of $d+l$-threitol and *meso*-erythritol in the aerosol phase during the photooxidation of 1,3-butadiene. In terms of the RO_2+RO_2 reactions, the major difference between isoprene and 1,3-butadiene is the presence of a tertiary carbon in isoprene which can influence the rate constant for the process involving tertiary radicals. Angove et al. (2006) detected the tetrols in NO_x experiments but after the time when NO would have been removed by reaction. Assuming the 2-methyl tetrols and tetrols form in the isoprene and 1,3-butadiene systems, respectively, partitioning from the gas to particle phase might be expected to be highly efficient, leading to the compounds being detected in the particle phase. Thus, photooxidation products which might be minor constituents of the gas phase could, on a relative basis, be more important constituents of the particle phase given the lower organic mass in the particle phase.

In an attempt to support the mechanism in Scheme 1, a chromatographic examination was made for a C_5-keto triol product formed by Reaction 5. Such a compound would have a molecular weight of 134 Da and a derivative molecular weight of 350 Da. A candidate peak was detected in the gas phase denuder sample in Experiment 1, having a reasonably consistent retention time and mass spectra for the co-product, but the compound could not be confirmed in the other experiments. Moreover, there was no evidence of the compound in the particle phase, as might be anticipated. Thus, there is no clear evidence for the presence of such a co-product. It is possible that the co-product, if formed, was rapidly photolyzed or involved in a secondary reaction, possibly oligomerization, removing the compound from the



Scheme 1. Possible mechanism for the formation of the methyl tetrols in the absence of NO_x and acidic sulfate seed aerosol.

system. Of course, an alternative explanation would be that the 2-methyl tetrols are formed through homogeneous reactions not represented by Scheme 1.

While the RO_2+RO_2 reactions for trihydroxy compounds could be enhanced for β-hydroxy peroxy radicals, the RO_2+HO_2 reaction is still probably the more significant channel. A reaction of the trihydroxy peroxy radical(s) formed in Reaction 4 might be expected to react with HO_2 to give C_5-hydroperoxides which could partition into the particle phase. Measurement of the organic peroxides in the particle phase indicated that approximately one-quarter of the aerosol mass was due to organic peroxides, most likely organic hydroperoxides. (This mass fraction is dependent on an extinction coefficient being equivalent to benzoyl peroxide at 470 nm and an assumed molecular weight of 150 g mol^{-1}. For lower assumed molecular weights the fraction would decrease proportionately.) The fraction of organic peroxide formed in the photooxidation of isoprene in the absence of NO_x is highly consistent with that found by Surratt et al. (2006) who reported organic peroxide values of 25–30% of the SOA for measurements conducted in the presence of seed aerosol. Finally, while there is no reported evidence for the conversion of C_5-trihydroxy hydroperoxides into TMS-derivatives identical to those formed from the 2-methyl tetrols, the possibility cannot be completely eliminated.

The aerosol parameters measured here can also be compared with previously reported studies. At present, SOA yields from the isoprene photooxidation system without NO_x have only been reported by Kroll et al. (2006). Those yields were determined from conventional batch-mode irradiations of isoprene and H_2O_2 using an SMPS to measure the aerosol volume with a measured density of 1.25 to convert aerosol volume to mass. Kroll et al. (2006) used initial H_2O_2-to-isoprene ratios one to two orders of magnitude higher than those employed in this work. This allowed the $OH+H_2O_2 \rightarrow HO_2+H_2O$ reaction to compete effectively with the isoprene + OH reaction and generating a system rich in HO_2. Kroll et al. (2006) also report a rapid decay of the SOA mass during the irradiation, which they attributed to chemical reactions of semivolatile components, possibly organic hydroperoxides, potentially from a mechanism as described by Molina et al. (2004). Aerosol yields ranging from 0.009 to 0.036 were reported in that study which for the same aerosol mass are much higher than those reported here. However, these differences could be attributed to a possibly greater extent of reaction and different SOA products in the Kroll et al. work. In addition, given radiation distribution used here, some of the organic peroxides might have undergone photolysis possibly lowering the condensable mass. However, yields from this work (SOA and SOC) have been determined using completely different approaches in the chamber operation (steady-state mode) and in the aerosol parameters measured (gravimetric SOA and SOC masses) and thus represent independent determinations from previous studies. Moreover, while SOA yields were obtained at aerosol masses approximately 2–5 times higher than Kroll et al. (2006), they were within the ranges of aerosol masses reported in other studies of the isoprene SOA yield (Dommen et al., 2006). SOC yields have not been presented prior to this work.

The effective enthalpy of vaporization was measured for isoprene SOA formed in both the presence and absence of NO_x. The composite organic aerosol is comprised of polyols, organic acids (e.g. 2-MGA), and other higher molecular weight oligomeric constituents which have previously been detected in isoprene SOA (Kalberer et al., 2006). As a result, the value for ΔH^{eff}_{vap} for the composite aerosol will be substantially less than what would likely be measured for individual chemical compounds associated with isoprene SOA. However, there are no measured enthalpies of formation for even minor constituents, such as 2-MGA or the 2-methyl tetrols. The data shows an average value for ΔH^{eff}_{vap} somewhat higher (43.2 kJ mol^{-1}) from the system with NO_x compared to that without NO_x (38.4 kJ mol^{-1}) suggesting minor differences in the volatility changes with temperature of the SOA constituents of either system. However, this difference is at the limit of being statistically significant compared to the 2-σ errors of the slopes (12%) for ΔH^{eff}_{vap} (Fig. 1). Henze and Seinfeld (2006), in modeling the contribution of isoprene SOA in the lower troposphere, estimated a value of 42 kJ mol^{-1} based largely on the data analysis of Chung and Seinfeld (2002). Thus, values reported in this work support the enthalpies of formation already being used in some modeling studies.

OM-to-OC ratios for isoprene SOA in the absence of NO_x (1.9) were found to be higher than for system without NO_x (1.5). The less volatile SOA is due possibly to the higher oxygen content of compounds formed from increased peroxy radical reactions for systems without NO_x. The lower OM/OC value for this system is also consistent with the lower effective enthalpy of vaporization. The data can be compared to recent measurement of OM/OC for the isoprene/NO_x system (Aiken et al., 2008). The initial isoprene and nitrogen oxides were within a factor of two of the initial concentrations in this study. Although the exact measurement conditions were not specified, the resulting OM/OC of 1.75 is approximately at the midpoint of the values reported here with and without NO_x.

Mass fractions of the isoprene tracers to the isoprene SOA were determined to provide a connection between the field and laboratory data. While it is not possible to accurately represent the range of atmospheric conditions present when ambient samples are taken, these fractions should provide an indicator to the relative importance of various SOA precursors. The previous work of Kleindienst et al. (2007b) provided mass fractions for the isoprene photooxidation products in the presence of NO_x and SO_2, because of the limited availability of data from experiments without SO_2. For this work, independent measures of SOA and SOC have allowed mass fractions to be calculated for both parameters. The only values for mass fractions of the isoprene tracer compounds come from Kleindienst et al. (2007b) who report mass fractions for f_{SOA} and f_{SOC} of 0.06 and 0.15, respectively. However, that work required the addition of SO_2 to promote particle formation unlike the present experiments. The data in this study indicates that the isoprene tracer compounds as measured using BSTFA derivatization tend to scale with the SOA and SOC masses in these systems.

4.1 Atmospheric implications

The high relative abundance of the methyl tetrols and 2-MGA in atmospheric samples found in a wide range of locations suggest that these experiments may have high relevance to atmospheric scenarios. In past studies, substantial abundances of the methyl tetrols and the C_5-alkene triols were only detected in laboratory systems in the presence of acidic sulfate aerosol (Edney et al., 2005; Surratt et al., 2007; Böge et al., 2006; Wang et al., 2005). However, the degree to which a laboratory system in the absence of NO_x adequately represents ambient systems having high isoprene emissions and low NO_x levels is a considerably more complex issue given the number of possible reactions of the RO_2 radical, particularly with the HO_2 radical. In ambient air, there are a wide range of organic peroxy and hydroperoxy radicals that can react with either the C_5-unsaturated hydroxy peroxy radicals or the C_5 trihydroxy peroxy radicals described here. Under ambient conditions at low NO_x, HO_2 concentrations are generally sufficiently high to dominate the removal of RO_2 radicals. Miyoshi et al. (1994) have suggested that under typical low NO_x conditions HO_2 reaction with RO_2 is two orders of magnitude more important than the RO_2+RO_2 reaction.

For the C_5-unsaturated dihydroxy compounds readily detected in the laboratory, there is recent evidence that these C_5-methyl butenediol-TMS compounds may have also been detected from denuder samples of ambient air. An examination of gas phase samples from a field study in Research Triangle Park, NC in 2000 shows the derivative mass spectra consistent with two 2-methyl butenediols detected in this work (see Appendix A). Moreover, the discovery of 2-methyl tetrols in the Amazon rain forest (Claeys et al., 2004a) where high isoprene emissions are expected under conditions with low levels of NO_x and SO_2 (thus acidic aerosol) would suggest that the current results may be applicable, under conditions where the concentrations of HO_2 radicals and of cross reactions involving other RO_2 radicals may be low. However, recent studies have shown that HO_x concentrations in forested areas tend to be higher than model simulations predict (Ren et al., 2008) and thus HO_2 radicals should be readily available. Other studies have also shown the regeneration of HO_x radicals from hydroperoxy precursors in tropical forested environments (Lelieveld et al., 2008). Therefore, under tropical forest conditions such as the Amazon, a possible explanation might be that C_5-trihydroxy hydroperoxides (or C_5 dihydroxy dihydroperoxide) are formed in the air from RO_2+HO_2, collected in the particle phase, and subsequently converted on the filter (perhaps by a hydrolysis reaction associated with the aerosol liquid water) to the 2-methyl tetrols which are then measured by the standard TMS derivatization techniques. An analogous mechanism has been suggested by Sato (2008) for the conversion of C_5 nitroxy triols to the 2-methyl tetrols in laboratory experiments at high NO_x levels. At the present time, direct analytical techniques are not readily available for analyzing polyfunctional hydroperoxides, although recent progress on atmospheric measurements of hydroperoxides has been made (Crounse et al., 2006). At present, the exact forms of precursors which derivatize to form methyl tetrol-TMS compounds still have considerable uncertainty and additional laboratory and field experiments will be required.

5 Summary

The present study has been conducted to examine the formation of isoprene organic aerosol and the isoprene tracer compounds (2-MGA, 2-methyltreitol, and 2-methylerythritol) in irradiations in the absence of NO_x. These experiments are designed to aid in understanding the formation of the 2-methyl tetrols under remote or tropical conditions where NO_x and SO_2 are typically at low atmospheric mixing ratios. An examination of the gas phase showed the presence of several 2-methyl butenediols, a result consistent with the findings of Ruppert and Becker (2000). In the particle phase, 2-methylglyceric acid, the two 2-methyl tetrols, and three alkenetriols were readily formed in the absence of acidic sulfate aerosol, in contrast to other recent laboratory studies. However, the experiments were carried out under relatively low H_2O_2 conditions which severely limited the production of HO_2 by means other than from RO reactions. These findings assume there are no artifacts created by the sampling and analytical methods.

A number of aerosol parameters were determined for the first time in the isoprene photooxidation system without NO_x. SOA/SOC, an important parameter to convert SOA into SOC in air quality models for comparison with field data, was found to average 1.9 in the absence of NO_x. The effective enthalpy of vaporization was measured as 38.6 kJ mol^{-1}, consistent with values that have previously been used in modeling studies. The yields in this work are lower than those of Kroll et al. (2006) for the same aerosol masses. SOC yields are also reported in this work and range from 0.5–1.4% for carbon masses between 17 and 49 μgC m^{-3}.

6 Note added in proof

Following the review of this paper, a study by F. Paulot et al. (Science, 325, 730–733, 2009) appeared that provides strong evidence for the formation of C_5-dihydroxy epoxides in the isoprene photooxidation system in the absence of NO_x. While Paulot et al. used substantially higher H_2O_2-to-isoprene ratios (creating an HO_2 rich system) than used in this work, the findings are potentially relevant to the present study. In particular, HO_2 formed could have reacted with the products of the OH+2-methyl hydroxybutene-hydroperoxides generated in Reaction (3) leading to the production of one or more C_5-dihydroxy epoxides in the gas phase. It is possible that the C_5-dihydroxy epoxides could be precursors of the 2-methyl tetrols (E. C. Minerath, M J. Elrod, Environ. Sci. Technol., 43, 1386–1391, 2009), although the absence of acidic aerosol together with the dry experimental conditions used might argue against it. Clearly, the role of the dihydroxy epoxides in forming the isoprene tracer compounds (2-MT and 2-ME) must be explored.

7 Disclaimer

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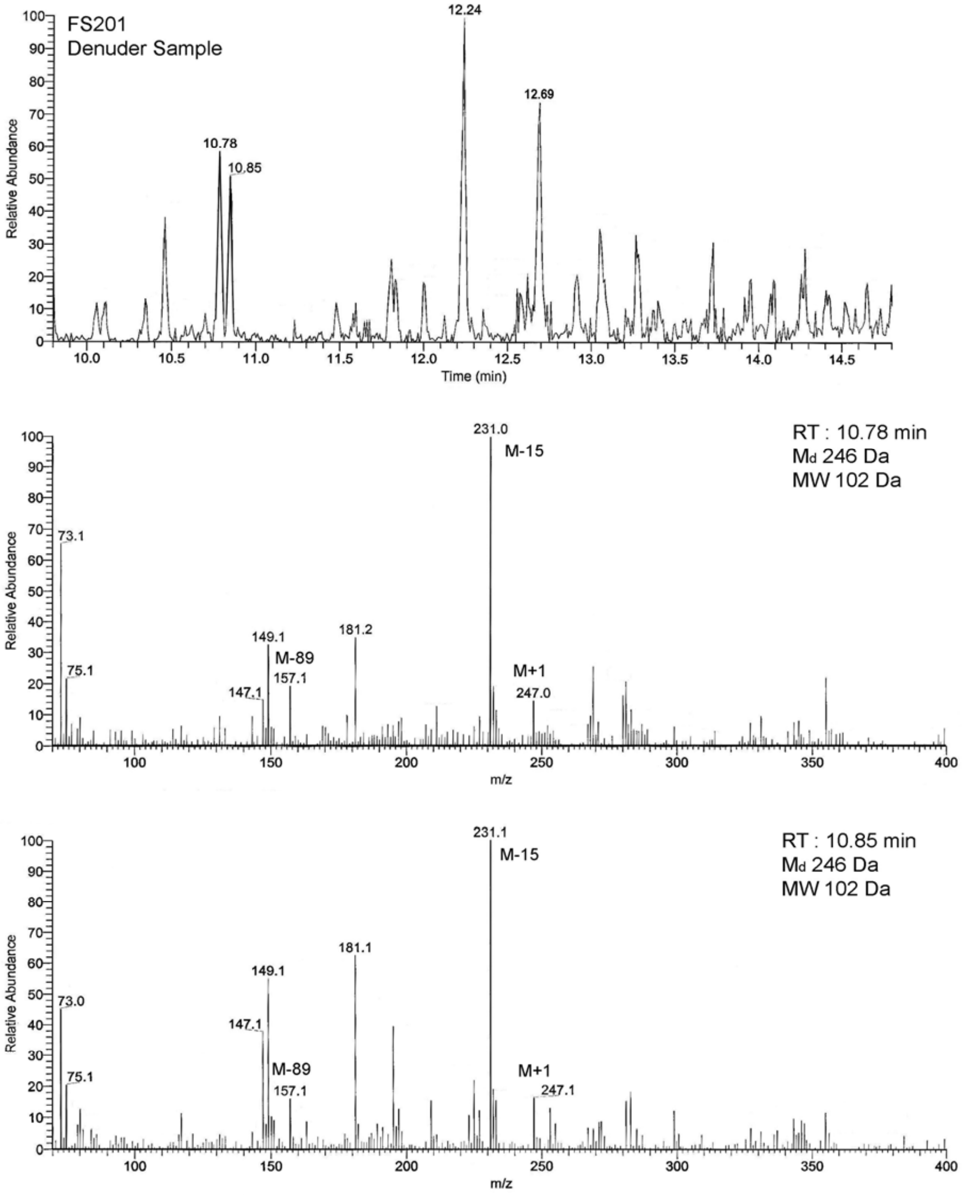

Fig. A1. Gas phase chromatograms and mass spectrum of the butenediols for Sample FS201 as described by Edney et al. (2003). The methyl butenediols are found at retention times of 10.78 and 10.85 min. For clarity, the selected ion chromatogram for m/z 231 is shown in the top panel. Experimental details and terminology used for the figure are the same as that in Edney et al. (2003).

Appendix A

Tentative identification of C_5-butenediol-TMS compounds in ambient samples

Ruppert and Becker (2000) originally detected the formation 2-methyl-3-butene-1,2-diol and 3-methyl-3-butene-1,2-diol in laboratory experiments of the photooxidation of isoprene in the absence of NO_x. For that measurement, air samples were bubbled in methanol and analyzed by GC-FID and GC-MS. The diols from the laboratory samples were compared by retention time and mass spectrum to the pure compounds synthesized in the laboratory. For this work as seen in Fig. 2, GC-MS chromatographs of four compounds found in the gas phase and having derivative molecular weights of 246 Da were consistent with those findings. In past (although not recent) field studies from this laboratory, sampling configurations were deployed in which both the gas- and particle-phase samples of ambient air were collected for chemical analysis. Edney et al. (2003) described in detail polar organic compounds collected at a field site in Research Triangle Park, NC in 2000. The GC-MS data from the denuder extract, representing the gas phase and taken prior to the particle-phase sample (Sample FS201), was recently re-evaluated for the presence of compounds consistent with methyl butenediol trimethylsilyl (TMS) derivatives. The details of the experimental procedure are given in Edney et al. (2003).

The chromatogram of the denuder sample is shown in Fig. A1 for retention times before the elution of 2-methylthreitol. The selected ion trace of the m/z 231 ion shows the presence of two peaks. While the chromatography from Edney et al. (2003) was considerably more compressed than that used in this study, the relative retention times and mass spectra for the two peaks in Fig. A1 (RT: 10.78 and 10.85 min) are highly consistent with the initial two peaks found in Fig. 2, which have been associated with the methyl butenediols as described in the text. In Fig. A1, while a number of peaks had the m/z 231 ion present, only for the two peaks being considered, the mass spectra of which are shown in Panels (b) and (c), is m/z 231 the base ion. Moreover, the relative intensities of the base ion to the minor ions (m/z 157, 73, and 247) appear to be consistent between the laboratory and field samples. One discrepancy between the laboratory and field mass spectra lie in the relative intensities of the m/z 147 and 149 ions, where in the laboratory samples, the m/z 147 ion generally has a greater intensity. Such differences for minor ions in laboratory and field samples are often seen and have been reported (Kleindienst et al., 2004). While there are a number of interfering ions in the mass spectra of the field sample, most of the characteristics are very consistent with the laboratory sample. Due to the 275 m^3 air volume collected, sample breakthrough of gas-phase species very likely occurred and thus quantitative values, even on a relative basis, are not possible to determine. While experimental conditions used herein appears to have allowed the formation of the methyl butenediols, HO_2 concentrations under atmospheric conditions are generally sufficiently high to render RO_2+RO_2 reactions as inconsequential. Thus, it is possible that the observed methyl butenediol-TMS derivatives could have formed from gas-phase precursors other than the methyl butenediols themselves. Nine sampling periods were taken in 2000 and 2001 in RTP, NC with evidence for the methyl butenediol-TMS derivatives being seen in four of the samples.

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References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., et al.: O/C and O/M ratios of primary, secondary and ambient organic aerosol with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478–4485, 2008.

Angove, D. E., Fookes, C. J. R., Hynes, R. G., Walters, C. K., and Azzi, M.: The characterization of secondary organic aerosol formed during the photodecomposition of 1,3-butadiene in air containing nitric oxide, Atmos. Environ., 40, 4597–4607, 2006.

Barnes, I., Becker, K. H., and Ruppert, L.: FTIR product study of the self-reaction of β-hydroxyethyl peroxy radicals, Chem. Phys. Lett., 203, 295–301, 1993.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Tech., 25, 221–241, 1996.

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., 40, 2501–2509, 2006.

Carter, W. P. L. and Atkinson, R.: Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, Int. J. Chem. Kinet., 28, 497–530, 1996.

Chung, S. H. and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosol, J. Geophys. Res., 107, 4407, doi:10.1029/2001JD001397, 2002.

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, 303, 1173–1176, 2004a.

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

Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry, Anal. Chem., 78, 6726–6732, 2006.

Docherty, K. S., Wu, W., Lim, Y. B., and Ziemann, P. J.: Contribution of organic peroxides to secondary organic aerosol formed from reactions of monoterpenes with O_3, Environ. Sci. Technol., 39, 4049–4059, 2005.

Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M. R., Gascho, A., Weingartner, E., Prevot, A. S. H., Verheggen, B., and Baltensperger U.: Laboratory observations of oligomers in the aerosol from isoprene/NO_x photooxidation, Geophys. Res. Lett., 33, L13805, doi:10.1029/2006GL026523, 2006.

Edney, E. O., Kleindienst, T. E., Conver, T. S., McIver, C. D., Corse, E. W., and Weathers, W. S.: Polar organic oxygenates in $PM_{2.5}$ at a southeastern site in the United States, Atmos. Environ., 37, 3947–3956, 2003.

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/NO_x/SO_2/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern US, Atmos Environ., 39, 5281–5289, 2005.

Fan, J. and Zhang, R.: Atmospheric oxidation mechanism of isoprene, Environ. Chem., 1, 140–149, 2004.

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. 100, 8873–8892, 1995.

Gundel, L. A., Lee, V. C., Mahanama, K. R. R., Stevens, R. K., and Daisey, J. M.: Direct determination of the phase distribution of semi-volatile polycyclic aromatic hydrocarbons using annular denuders, Atmos. Environ., 29, 1719–1733, 1995.

Henze, D. K. and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, Geophys. Res. Lett., 33, L09812, doi:10.1029/2006GL025976, 2006.

Hu, D., Bian, Q., Li, T. W. Y., Lau, A. K. H., and Yu, J. Z.: Contributions of isoprene, monoterpenes, β-caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006, J. Geophys. Res., 113, D22206, doi:10.1029/2008JD010437, 2008.

Ion, A. C., Vermeylen, R., Kourtchev, I., Cafmeyer, J., Chi, X., Gelencsér, A., Maenhaut, W., and Claeys, M.: Polar organic compounds in rural $PM_{2.5}$ aerosols from K-puszta, Hungary, during a 2003 summer field campaign: Sources and diel variations, Atmos. Chem. Phys., 5, 1805-1814, 2005, http://www.atmos-chem-phys.net/5/1805/2005/.

Jaoui, M., Edney, E. O., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Surratt, J. D., and Seinfeld, J. H.: Formation of secondary organic aerosol from irradiated α-pinene/toluene/NO_x mixtures and the effect of isoprene and sulfur dioxide, J. Geophys. Res., 113, D09303, doi:10.1029/2007JD009426, 2008.

Jaoui, M., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic and/or hydroxyl groups, 1, Method development, Anal. Chem., 76, 4765–4778, 2004.

Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups, 2, Organic tracer compounds from monoterpenes, Environ. Sci. Technol., 39, 5661–5673, 2005.

Jenkin, M. E. and Hayman, G. D.: Kinetics of reactions of primary, secondary, and tertiary β-hydroxy peroxy radicals: application to isoprene degradation, J. Chem. Soc. Faraday Trans., 91, 1911–1922, 1995.

Jenkin, M. E., Boyd, A. A., and Lesclaux, R.: Peroxy radical kinetics resulting from the OH-initiated oxidation of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and isoprene, J. Atmos. Chem., 29, 267–298, 1998.

Kalberer, M., Sax, M., and Samburova, V.: Molecular size evolution of oligomers in organic aerosols collected in urban atmospheres and generated in a smog chamber, Environ. Sci. Technol., 40, 5917–5922, 2006.

Kleindienst, T. E., Conver, T. S., McIver, C. D., and Edney, E. O.: Determination of secondary organic aerosol products from the photooxidation of toluene and their implication in $PM_{2.5}$, J. Atmos. Chem., 47, 79–100, 2004.

Kleindienst, T. E., Edney, E. O., Lewandowski, M., Offenberg, J. H., and Jaoui, M.: Secondary organic carbon and aerosol yields from the irradiations of isoprene and α-pinene in the presence of NO_x and SO_2, Environ. Sci. Technol., 40, 3807–3812, 2006.

Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Jaoui, M., and Edney, E. O.: Ozone-isoprene reaction: Reexamination of the formation of secondary organic aerosol, Geophys. Res. Lett., 34, L01805, doi:10.1029/2006GL027485, 2007a.

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location, Atmos. Environ., 41, 8288–8300, 2007b.

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, Finland, Atmos. Chem. Phys., 5, 2761–2770, 2005, http://www.atmos-chem-phys.net/5/2761/2005/.

Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T., and Claeys, M.: Polar organic marker compounds in $PM_{2.5}$ aerosol from a mixed forest site in western Germany, Chemosphere, 73, 1308–1314, 2008.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from the photooxidation of isoprene under high NO_x conditions, Geophys. Res. Lett., 32, L18808, doi:10.1029/2005GL023637, 2005.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from photooxidation of isoprene, Environ. Sci. Technol., 40, 1869–1877, 2006.

Lane, T. E. and Pandis, S. N.: Predicted secondary organic aerosol concentration from the oxidation of isoprene in the Eastern United States, Environ. Sci. Technol., 41, 3984–3990, 2007.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, 2008.

Lewandowski, M., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Sheesley, R. J., and Schauer, J. J.: Primary and secondary contribution to ambient PM in the Midwestern United States, Environ. Sci. Technol., 42, 3303–3309, 2008.

Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F.: Organic peroxy radicals: Kinetics, spectroscopy and tropospheric chemistry, Atmos. Environ., 26A, 1805–1961, 1992.

Matsunaga, S. N., Wiedinmyer, C., Guenther, A. B., Orlando, J. J., Karl, T., Toohey, D. W., Greenberg, J. P., and Kajii, Y.: Isoprene oxidation products are a significant atmospheric aerosol component, Atmos. Chem. Phys. Discuss., 5, 11143–11156, 2005, http://www.atmos-chem-phys-discuss.net/5/11143/2005/.

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

Molina, M. J., Ivanov, A. V., Trakhtenberg, S., and Molina, L. T.: Atmospheric evolution of organic aerosol, Geophys. Res. Lett., 31, L22104, doi:10.1029/2004GL020910, 2004.

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3), Atmos. Chem. Phys., 8, 4117–4140, 2008, http://www.atmos-chem-phys.net/8/4117/2008/.

Offenberg, J. H., Kleindienst, T. E., Jaoui, M., Lewandowski, M., and Edney, E. O.: Thermal properties of secondary organic aerosol, Geophys. Res. Lett., 33, L03816, doi:10.1029/2005GL024623, 2006.

Paulsen, D., Weingartner, E., Alfarra, M. R., and Baltensperger, U.: Volatility measurements of photochemically and nebulizer-generated organic aerosol particles, J. Aerosol Sci., 37, 1025–1051, 2006.

Ren, X., Olson, J. R., Crawford, J. H., et al.: HO_x chemistry during INTEX-A 2004: Observations, model, calculation, and comparison with previous studies, J. Geophys. Res., 113, D05310, doi:10.1029/2007JD009166, 2008.

Ruppert, L. and Becker, K. H.: A product study of the OH radical-initiated oxidation of isoprene: formation of C_5-unsaturated diols, Atmos. Environ., 34, 1529–1542, 2000.

Russell, G. A.: Deuterium-isotope effects in the autooxidation of aralkyl hydrocarbons: Mechanism of the interaction of peroxy radicals, J. Amer. Chem. Soc., 79, 3871–3877, 1957.

Sato, K.: Detection of nitrooxypolyols in secondary organic aerosol formed from the photooxidation of conjugated dienes under high-NO_x conditions, Atmos. Environ., 42, 6851–6861, 2008.

Scanlon, J. T. and Willis, D. E.: Calculation of flame ionization detector ionization relative response factors using the effective carbon number concept, J. Chromatogr. Sci., 23, 333–340, 1985.

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 composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110, 9665–9690, 2006.

Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Affect of acidity on secondary organic aerosol formation from isoprene, Environ. Sci. Technol., 41, 5363–5369, 2007.

Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilyation and gas chromatography/ion trap mass spectrometry, J. Mass Spectrom., 42, 101–116, 2007.

van Donkelaar, A., Martin, R. V., Park, R. J., Heald, C. L., Fu, T.-M., Liao, H., and Guenther, A.: Model evidence for a significant source of secondary organic aerosol from isoprene, Atmos. Environ., 41, 1267–1274, 2007.

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

Zhang, Y., Huang, J.-P., Henze, D. K., and Seinfeld, J. H.: Role of isoprene in secondary organic aerosol formation on a regional scale, J. Geophys. Res., 112, D20207, doi:10.1029/2007JD008675, 2007.

Zhao, J., Zhang, R., Fortner, E. C., and North, S. W.: Quantification of hydroxycarbonyls from OH – isoprene reactions, J. Amer. Chem. Soc., 126, 2686–2687, 2004.