

Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃)

N. L. Ng¹, A. J. Kwan², J. D. Surratt¹, A. W. H. Chan¹, P. S. Chhabra¹,
A. Sorooshian¹, H. O. T. Pye¹, J. D. Crouse¹, P. O. Wennberg^{2,3}, R. C. Flagan^{1,2},
and J. H. Seinfeld^{1,2}

¹Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, CA 91125, USA

²Division of Engineering and Applied Science, California Institute of Technology, Pasadena,
CA 91125, USA

³Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena,
CA 91125, USA

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Correspondence to: J. H. Seinfeld (seinfeld@caltech.edu)

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Abstract

Secondary organic aerosol (SOA) formation from the reaction of isoprene with nitrate radicals (NO₃) is investigated in the Caltech indoor chambers. Experiments are performed in the dark and under dry conditions (RH<10%) using N₂O₅ as a source of NO₃ radicals. For an initial isoprene concentration of 18.4 to 101.6 ppb, the SOA yield (defined as the ratio of the mass of organic aerosol formed to the mass of parent hydrocarbon reacted) ranges from 4.3% to 23.8%. By examining the time evolutions of gas-phase intermediate products and aerosol volume in real time, we are able to constrain the chemistry that leads to the formation of low-volatility products. Although the formation of ROOR from the reaction of two peroxy radicals (RO₂) has generally been considered as a minor channel, based on the gas-phase and aerosol-phase data it appears that RO₂+RO₂ reaction (self reaction or cross-reaction) in the gas phase yielding ROOR products is a dominant SOA formation pathway. A wide array of organic nitrates and peroxides are identified in the aerosol formed and mechanisms for SOA formation are proposed. Using a uniform SOA yield of 10% (corresponding to M₀≈10 μg m⁻³), it is estimated that ~2 to 3 Tg yr⁻¹ of SOA results from isoprene + NO₃. The extent to which the results from this study can be applied to conditions in the atmosphere depends on the fate of peroxy radicals (i.e. the relative importance of RO₂+RO₂ versus RO₂+NO₃ reactions) in the nighttime troposphere.

1 Introduction

Isoprene is the most abundant non-methane hydrocarbon emitted into the atmosphere with a global emission of ~500 Tg yr⁻¹ (Guenther et al., 1995, 2006). In the troposphere, isoprene reacts with hydroxyl radicals (OH), ozone (O₃), and nitrate radicals (NO₃). Owing to its high concentration and reactivity with OH radicals, isoprene plays an important role in the photochemistry occurring within the atmospheric boundary layer. Recently, it has been shown that the photooxidation of isoprene leads to the

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formation of low volatility species that condense to form SOA (Claeys et al., 2004; Edney et al., 2005; Kroll et al., 2005; Dommen et al., 2006; Kroll et al., 2006; Surratt et al., 2006); SOA yields as high as ~3% have been observed (Kroll et al., 2005, 2006). Global SOA production from isoprene photooxidation has been estimated to be about 13 Tg yr⁻¹ (Henze et al., 2007).

Although emission of isoprene from vegetation is triggered by sunlight and increases with light intensity and temperature (e.g. Sharkey et al., 1996), the isoprene mixing ratio has been observed to peak in early evening in several field studies, with a measured mixing ratio up to a few ppb (Curren et al., 1998; Starn et al., 1998; Stroud et al., 2002; Steinbacher et al., 2005). After sunset, the isoprene mixing ratio drops rapidly, and it has been suggested that the reaction with nitrate radicals, NO₃, is a major contributor to isoprene decay at night (Curren et al., 1998; Starn et al., 1998; Stroud et al., 2002; Steinbacher et al., 2005). Typical NO₃ radical mixing ratios in boundary layer continental air masses range between ~10 to ~100 ppt (Platt and Janssen, 1995; Smith et al., 1995; Heintz et al., 1996; Carslaw et al., 1997). However, concentrations as high as several hundred ppt have been observed over northeastern USA and Europe (Platt et al., 1981; von Friedeburg et al., 2002; Brown et al., 2006; Penkett et al., 2007). Given the rapid reaction rate between isoprene and NO₃ radicals ($k_{\text{NO}_3} = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298 \text{ K}$, IUPAC), it is likely that NO₃ radicals play a major role in the nighttime chemistry of isoprene.

The kinetics and gas-phase products of the isoprene-NO₃ reaction have been the subject of several laboratory and theoretical studies (Jay and Stieglitz, 1989; Barnes et al., 1990; Skov et al., 1992; Kwok et al., 1996; Berndt and Böge, 1997; Suh et al., 2001; Zhang et al., 2002; Fan et al., 2004). In many studies, C₅-nitroxy carbonyl is identified as the major first-generation gas-phase reaction product (Jay and Stieglitz, 1989; Skov et al., 1992; Kwok et al., 1996; Berndt and Böge, 1997). Other compounds such as C₅-hydroxynitrate, C₅-nitroxyhydroperoxide, and C₅-hydroxycarbonyl have also been identified (Kwok et al., 1996); C₅-hydroxynitrate has also been measured in ambient air with concentrations in the lower ppt range at a few ng m⁻³ (Werner

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et al., 1999). According to the experimental study by Barnes et al. (1990), the yield for nitrate-containing compounds from the reaction of isoprene and NO₃ radicals can be as high as 80%. A recent modeling study in conjunction with observations from the ICARTT field campaign suggests that ~50% of the total isoprene nitrates production occurs via reaction of isoprene and NO₃ radicals (Horowitz et al., 2007).

Little is known beyond the formation of the first-generation products of the reaction of NO₃ with isoprene. The isoprene nitrates and other first-generation products still contain a double bond, and it is likely that the further oxidation of these species will lead to low volatility products that can contribute to SOA formation at nighttime.

In this work, SOA formation from the reaction of isoprene with NO₃ radicals is investigated. Laboratory chamber experiments are performed in the dark using N₂O₅ as a source of NO₃ radicals. Aerosol yields are obtained over a range of initial isoprene concentrations (mixing ratios). By examining the time evolutions of aerosol volume and different intermediate gas-phase products, we are able to constrain the chemistry that leads to the formation of low-volatility products. Mechanisms for SOA formation are proposed and chemical composition data of the SOA formed are also presented.

2 Experimental section

Experiments are carried out in the Caltech dual 28 m³ Teflon chambers. A detailed description of the facility is provided elsewhere (Cocker et al., 2001; Keywood et al., 2004). Before each experiment, the chambers are flushed continuously for over 24 h. Aerosol number concentration, size distribution, and volume concentration are measured by a Differential Mobility Analyzer (DMA, TSI model 3081) coupled with a condensation nucleus counter (TSI model 3760). All aerosol growth data are corrected for wall loss, in which size-dependent particle loss coefficients are determined from inert particle wall loss experiments (Keywood et al., 2004). Temperature, relative humidity (RH), O₃, NO, and NO_x are continuously monitored. Experiments are performed in the dark at room temperature (20–21°C) and under dry conditions (RH < 10%).

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In most experiments, seed aerosols are introduced into the chamber to act as a substrate onto which the gas-phase products may condense. Seed aerosols are generated by atomizing an aqueous solution with a constant-rate atomizer. The seed solution consists of 0.015 M (NH₄)₂SO₄. In a few experiments, acidic seed is used, consisting of 0.03 M MgSO₄ and 0.05 M H₂SO₄. The initial particle number concentration is ~20 000 particles cm⁻³, with a geometric mean diameter of ~50 nm. The initial seed volume is 10–12 μm³ cm⁻³. In some experiments, no seed particles are added and aerosols are formed via nucleation. After introduction of the seed aerosols (in seeded experiments), a known volume of isoprene (Aldrich, 99%) is injected into a glass bulb and introduced into the chamber by an air stream. The mixing ratio of isoprene is monitored with a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent model 6890N). The column used is a bonded polystyrene-divinylbenzene based column (HP-PLOT Q, 15 m×0.53 mm, 40 μm thickness, J&W Scientific). The oven temperature is held at 60°C for 0.5 min, ramped at 35°C min⁻¹ to 200°C, and held constant for 3.5 min. The thermal decomposition of N₂O₅ serves as a source of NO₃ radicals in these experiments. N₂O₅ is prepared and collected offline by mixing a stream of nitric oxide (≥99.5%, Matheson Tri Gas) with a stream of ozone in a glass bulb (Davidson et al., 1978):

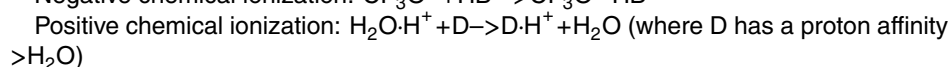
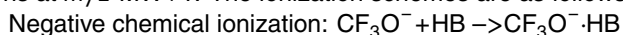


Ozone is generated by flowing oxygen through an ozonizer (OREC model V10-0, Phoenix, AZ) at ~1 L min⁻¹. The mixing ratio of ozone is measured by a UV/VIS spectrometer (Hewlett Packard model 8453) to be ~2%. The flow rate of nitric oxide into the glass bulb is adjusted until the brown color in the bulb disappears. The N₂O₅ is trapped for 2 h in an acetone-dry ice bath (approximately at -80°C; cold enough to trap N₂O₅ but not O₃, as condensed O₃ can explode upon warming and is extremely

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dangerous) as a white solid, and stored between experiments under liquid nitrogen temperature. Once the seed and isoprene concentrations in the chamber stabilize, reaction is initiated by vaporizing N₂O₅ into an evacuated 500 mL glass bulb and introduced into the chamber with an air stream of 5 L min⁻¹. The amount of N₂O₅ injected is estimated based on the vapor pressure in the glass bulb, which is measured using a capacitance manometer (MKS); this amount corresponds to an initial mixing ratio of ~1 ppm in the chamber. The thermal decomposition of N₂O₅ forms NO₂ and NO₃ radicals. Impurities in the N₂O₅ starting material are quantified by FTIR spectroscopy (Nicolet model Magna 550). N₂O₅ is vaporized into an evacuated pyrex cell (18 cm in length and 300 cm³) with CaF₂ windows. Spectra are collected immediately upon addition over the 1000 cm⁻¹ to 4000 cm⁻¹ window allowing for quantification of NO₂ (1616 cm⁻¹ band) and HNO₃ (3550 cm⁻¹ band) impurities.

A custom-modified Varian 1200 Chemical Ionization Mass Spectrometer (CIMS) is used to continuously monitor the concentrations of various gas-phase intermediates and products over the course of the experiments. The CIMS instrument is operated mainly in negative mode using CF₃O⁻ as a reagent ion, which selectively clusters with compounds having high fluorine affinity (e.g., acidic compounds and many hydroxy- and nitroxy- carbonyls), forming ions at *m/z* MW+85. In some experiments, the CIMS instrument is also operated in the positive mode using H₂O·H⁺ as a reagent ion forming ions at *m/z* MW+1. The ionization schemes are as follows:



The term “product ion” is used throughout this manuscript to describe the ionized products formed through the above chemical reaction schemes. Typically, we scan from *m/z* 50 to 400. More details about the CIMS technique are given in Crouse et al. (2006) and Ng et al. (2007a). Because authentic standards are not available for most of the major products, sensitivities have been estimated from calibration of similar species (Crouse et al., 2006).

Aerosol physical and chemical properties are monitored by many instruments. Real-time particle mass spectra are obtained with an Aerodyne quadrupole Aerosol Mass Spectrometer (Q-AMS) (Jayne et al., 2000). A Particle-Into-Liquid Sampler (PILS, Brechtel Manufacturing, Inc.) coupled with ion chromatography (IC) is employed for quantitative measurements of water-soluble ions in the aerosol phase (Sorooshian et al., 2006). Duplicate Teflon filters (PALL Life Sciences, 47-mm diameter, 1.0- μm pore size, teflo membrane) are collected from a selected number of experiments for offline chemical analysis. Filter sampling is initiated when the aerosol volume reaches its maximum value. Depending on the total volume concentration of aerosol in the chamber, the filter sampling time is 2–4 h, which results in $\sim 2\text{--}5\text{ m}^3$ of total chamber air sampled. Teflon filters used for high-resolution electrospray ionization-time-of-flight mass spectrometry (ESI-TOFMS) analysis are extracted in 5 mL of high-purity methanol (LC-MS CHROMASOLV-Grade, Sigma-Aldrich) by 45 min of sonication. Methanol sample extracts are then blown dry under a gentle N_2 stream (without added heat) once the filters are removed and archived at -20°C . Dried residues are then reconstituted with 500 mL of a 1:1 (v/v) solvent mixture of 0.1% acetic acid in water (LC-MS CHROMASOLV-Grade, Sigma-Aldrich) and 0.1% acetic acid in methanol (LC-MS CHROMASOLV-Grade, Sigma Aldrich). All resultant filter extracts are analyzed by a Waters ACQUITY ultra performance liquid chromatography (UPLC) system, coupled to a Waters LCT Premier XT time-of-flight mass spectrometer (TOFMS) equipped with an ESI source that is operated in the negative (-) ionization mode. Detailed operating conditions for the UPLC/(-)ESI-TOFMS instrument have been described previously (Ng et al., 2007a). A Waters ACQUITY UPLC HSS column is selected to separate the SOA components because of its increased retention of water-soluble polar organics; separation is achieved as a result of trifunctionally-bonded (T3) C_{18} alkyl residues on this column, which prevent stationary phase collapse when a 100% aqueous mobile phase is used and result in better retention of water-soluble polar organic compounds. In addition to the UPLC/(-)ESI-TOFMS analysis, all remaining Teflon filters are extracted and analyzed for total peroxide content (sum of ROOR and ROOH) by using an iodometric-

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spectroscopic method previously described by Surratt et al. (2006).

To study the mechanism of SOA formation, in several experiments the experimental protocols are slightly modified: (1) An excess amount of isoprene (relative to N_2O_5 concentration) is injected into the chamber to prevent the further reaction of first-generation gas-phase products, allowing these products to be detected more readily; (2) After the addition of isoprene, pulses of N_2O_5 are introduced into the chamber to study the evolution of different intermediate gas-phase products; (3) With isoprene well mixed in the chamber, N_2O_5 is introduced slowly to maximize the self-reaction of peroxy radicals (see Sect. 4.2). This is achieved by first injecting N_2O_5 into a 65 L Teflon bag; then an air stream of 1 L min^{-1} is passed through the Teflon bag to introduce N_2O_5 into the chamber over a 7-h period. We refer to this as the “slow N_2O_5 injection experiment”; and (4) With N_2O_5 well mixed in the chamber, isoprene is introduced slowly to maximize the reaction between peroxy radicals and nitrate radicals (see Sect. 4.2). This is achieved by first injecting isoprene into a 65 L Teflon bag, and then introduced into the chamber with an air stream of 0.1 L min^{-1} for 7 h. We refer to this as the “slow isoprene injection experiment”.

Experimental conditions and results are given in Table 1. In calculating SOA yield (defined as the ratio of the organic aerosol mass formed to the mass of parent hydrocarbon reacted), knowledge of the SOA density is required. By comparing volume distributions from the DMA and mass distributions from the Q-AMS, the effective density for the SOA formed can be estimated (Bahreini et al., 2005; Alfara et al., 2006).

3 Results

3.1 Blank experiments

Blank experiments are performed to ensure that the aerosol growth observed is from the reaction of isoprene with NO_3 radicals. In these experiments, $\sim 1\text{ ppm}$ N_2O_5 is introduced into chamber after the addition of ammonium sulfate seed aerosol (with no

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isoprene present). As shown in Fig. 1, aerosol volume increases by $\sim 2 \mu\text{m}^3 \text{ cm}^{-3}$ within an hour after the introduction of N_2O_5 . About $2.5 \mu\text{g m}^{-3}$ of inorganic nitrate is measured by PILS/IC, which agrees well with the amount of nitrates detected by Q-AMS. FTIR analysis indicates the presence of $\sim 10\%$ HNO_3 and 4% NO_2 impurity in the N_2O_5 prepared, thus the nitrates measured by PILS/IC and Q-AMS likely arise from the partitioning or reactive uptake of gas-phase HNO_3 into the aerosol phase, or HNO_3 produced from heterogeneous hydrolysis of N_2O_5 . As in the Q-AMS analysis, no organic species are detected in the filter samples collected from these blank experiments.

3.2 Aerosol yields

A series of experiments with different initial isoprene concentrations are carried out (these are referred to as “typical yield experiments” hereafter). The initial isoprene concentration ranged from 18.4 to 203.4 ppb. Figure 2 shows the reaction profile of the oxidation of an initial mixture containing 203.4 ppb isoprene. Since the chamber is NO_x -free at the beginning of the experiment, once N_2O_5 is introduced into the chamber the equilibrium in Reaction (3) favors the formation of NO_3 . This generates a relatively high concentration of NO_3 radicals and results in rapid isoprene decay. Aerosol growth is observed and aerosol volume continues to increase even after all the isoprene is consumed. Owing to the rapid isoprene decay and the relatively long time between each GC measurement (12 min), the isoprene decay over time is captured only in experiments in which the initial isoprene concentration is >100 ppb. Based on the observed isoprene decay in these experiments and the isoprene- NO_3 rate constant k_{NO_3} , the NO_3 concentration in the chamber is estimated to be ~ 140 ppt.

The SOA yield of each experiment (Table 1) is shown in Fig. 3. The density of the SOA is determined to be 1.42 g cm^{-3} . The amount of inorganic nitrate detected by PILS/IC in each experiment ranges from 1.6 to $2.6 \mu\text{g m}^{-3}$, which is approximately equal to that measured in the blank experiments. In calculating SOA yield, the organic

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aerosol mass is corrected for the amount of inorganic nitrate measured in each experiment. For convenience, SOA yields can be parameterized by a semi-empirical model based on absorptive gas-particle partitioning of two semivolatile products (Odum et al., 1996, 1997ab):

$$Y = \Delta M_o \left[\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o} \right] \quad (4)$$

in which Y is the aerosol yield, ΔM_o is the organic aerosol mass produced, M_o is the organic aerosol mass present (equal to ΔM_o in chamber experiments with no absorbing organic mass present initially), α_i is the mass-based gas-phase stoichiometric fraction for semivolatile species i , and $K_{om,i}$ is the gas-particle partitioning coefficient for species i . With this two-product model, Eq. (4) is fit to the experimental yield data (data with $\Delta M_o < 100 \mu\text{g m}^{-3}$) and the yield parameters obtained are: $\alpha_1 = 0.089$, $\alpha_2 = 0.203$, $K_{om,1} = 0.182 \text{ m}^3 \mu\text{g}^{-1}$, and $K_{om,2} = 0.046 \text{ m}^3 \mu\text{g}^{-1}$. For an organic aerosol mass of $\sim 10 \mu\text{g m}^{-3}$, the aerosol yield is $\sim 10\%$.

Also shown in Fig. 3 are aerosol yields from the slow isoprene/ N_2O_5 injection experiments. Since the PILS/IC is not employed in these experiments, in calculating SOA yields it is assumed that the amount of inorganic nitrate formed in these slow injection experiments is roughly the same as that in other experiments. For the slow isoprene injection experiment, no isoprene is observed by GC-FID, indicating that once the isoprene enters the chamber, it is quickly consumed by reaction with NO_3 . The time profile of isoprene injection is obtained in a separate experiment, in which the same amount of isoprene is added into the chamber without N_2O_5 present. Assuming the amount of isoprene injected into the chamber is the same as the isoprene reacted, the amount of isoprene reacted over the course of the slow isoprene experiment can be deduced. As seen in Fig. 3, the SOA yield from the slow N_2O_5 injection experiment is roughly the same as those in the other yield experiments; the yield from the slow isoprene injection experiment, however, is lower.

The time-dependent “growth curves” (organic aerosol, ΔM_o , as a function of hydro-

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carbon reacted, ΔHC) over the course of the slow N_2O_5 injection experiment and the slow isoprene injection experiment are shown in Fig. 4. As hydrocarbon measurements are made with a lower frequency than particle volume, the isoprene concentrations shown are obtained by interpolating GC-FID measurements. In both experiments about 50 ppb of isoprene is consumed, the only difference being the order of isoprene/ N_2O_5 injection. From Fig. 4 it is clear that as the reaction proceeds, more aerosol is formed in the slow isoprene injection experiment for the same amount of isoprene reacted. However, the final SOA yield under the slow N_2O_5 injection conditions is higher due to continued aerosol formation even after the complete consumption of isoprene. The presence of a “hook” at the end of the growth curve for the slow N_2O_5 injection experiment indicates that further reactions are contributing to aerosol growth after isoprene is consumed (Ng et al., 2006). This is further discussed in Sect. 4.3.

3.3 Gas-phase measurements

The CIMS technique measures the concentrations of different gas-phase products over the course of the experiments. A series of experiments is carried out to study the mechanisms of SOA formation by varying the relative amount of isoprene and N_2O_5 injected and monitoring the time evolution of the intermediate products. Shown in Fig. 5 are the time profiles of three major gas-phase products and the corresponding aerosol growth from the excess isoprene experiment. In this experiment, ~ 120 ppb of N_2O_5 is first injected into the chamber, followed by the introduction of ~ 800 ppb isoprene. The initial concentration of isoprene is estimated based on the volume of the isoprene injected and the chamber volume. Once isoprene is injected, a number of product ions are formed immediately, with m/z 230, 232, and 248 being the most dominant ones. Several minor product ions at m/z 185, 377, and 393 are also observed (not shown). With the presence of excess isoprene, it is expected that the three major products detected are first-generation products. Their further reaction is suppressed, as indicated by the relatively constant concentrations of the product ions once they are formed. At the end of the experiment, 725 ppb of isoprene is measured by GC-FID.

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A small amount of aerosol is formed instantaneously, likely from the condensation of relatively nonvolatile first-generation products, or from further generation products that are formed at a very rapid rate.

To study further the evolution of the gas-phase products, an experiment is performed in which pulses of N_2O_5 are introduced into the chamber (with isoprene present) (Fig. 6). The top panel shows the isoprene decay and aerosol formation; the middle panel shows the time profiles of the three major first-generation products (m/z 230, 232, and 248); the bottom panel shows the time profiles of three minor products (m/z 185, 377, and 393). In this experiment, 179 ppb of isoprene is first injected into the chamber, followed by the addition of 3 pulses of N_2O_5 (~ 120 , 50, 210 ppb). The observations after the addition of the first pulse of N_2O_5 are similar to the excess isoprene experiment described above. With the addition of ~ 120 ppb N_2O_5 , 97 ppb of isoprene is reacted away, m/z 230, 232, and 248 are formed with concentrations of ~ 53 ppb, 25 ppb, and 21 ppb, respectively. Because of the lack of authentic standards, the concentrations are uncertain. Because the sum of the ion concentrations derived from our estimated sensitivities is equal to the reacted isoprene, our estimated sensitivity must represent a lower limit for the actual sensitivity of the CIMS technique to these compounds. Similar to the data in Fig. 5, the concentrations of these product ions stay relatively constant owing to the presence of excess isoprene. The minor products at m/z 185, 377, and 393, are formed with the concentrations of ~ 1.5 ppb, 1 ppb, and 1 ppb, respectively. It is noted that the m/z 393 ion is formed with a relatively slower rate than all other product ions. A small amount of aerosol is observed. At $t=15:40$, a second pulse of N_2O_5 (~ 50 ppb) is introduced into the chamber and the remaining 82 ppb isoprene is completely consumed. As seen from Fig. 6, the concentrations of all intermediate products increase accordingly and more aerosol is produced. The relative increase in the concentration of m/z 232 ion is not as high as would be expected if we assume the ratio of m/z 230 to 232 formed to be the same as in the first pulse of N_2O_5 addition (i.e. $\sim 2:1$). This indicates that some of m/z 232 ion has reacted with NO_3 radicals. The last pulse of N_2O_5 (~ 210 ppb) is added at $t=19:00$. Since all isoprene

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has been consumed, the additional NO_3 radicals react mainly with the first-generation products, as indicated by the decay of m/z 230, 232, and 248, 185, 377, and 393 ions. Of all of the observed products, it appears that m/z 232 and 377 ions are the most reactive with NO_3 radicals, and their decays in excess NO_3 are strongly correlated with aerosol growth. The rest of the product ions display relatively slower decay kinetics. The decay of the major product ion at m/z 230 does not appear to correlate with aerosol growth, as the concentration of the m/z 230 ion continues to decrease throughout the experiment but there is no further aerosol growth. Since the CIMS instrument has only 0.5 AMU resolution and it cannot distinguish products of similar or identical molecular weight, it is likely that many of observed ions comprise isomers formed from the NO_3 attack at different positions. The fact that many of the observed product ions show two distinct decay time scales indicates that these isomers have substantially different reactivity towards NO_3 radicals.

3.4 Chemical composition of SOA

3.4.1 Aerosol Mass Spectrometer (Q-AMS) measurements

Figure 7 shows the AMS spectrum of SOA formed in the typical yield experiments. Each mass fragment is normalized by the total signal. The SOA exhibits relatively high signals at m/z 30, 43, and 46. The signals at m/z 30 and 46 likely correspond to NO^+ (30) and NO_2^+ (46) fragments from the nitrates in the aerosol. The spectrum shown in Fig. 7 is obtained when aerosol volume reaches its maximum value; the spectrum obtained several hours after aerosol volume peaks shows minimal changes in the mass fractions of different fragments, indicating that the aerosol composition is not changing significantly over time.

Figure 8 shows the mass spectrum of the slow N_2O_5 injection experiment versus a typical yield experiment; Fig. 9 shows the mass spectrum of the slow isoprene injection experiment versus a typical yield experiment. As shown in both figures, the mass fragments fall on the 1:1 line, suggesting a similar SOA composition under the three

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different experimental conditions.

3.4.2 Offline chemical analysis

Figure 10 shows the representative UPLC/(–)ESI-TOFMS base peak ion chromatograms (BPCs) for different types of experiments conducted. The numbers denoted above the selected chromatographic peaks correspond to the most abundant negative ions observed in their respective mass spectra. Comparison of the BPCs shown in Fig. 10 indicates that the compositions of the SOA are quite similar for the typical yield experiment, slow isoprene injection experiment, and the acid seed experiment, suggesting a common SOA formation pathway. The SOA composition from the excess isoprene experiment, however, is different from these experiments. This will be discussed further in Sect. 4.4.

Accurate mass measurements for all ions observed by the UPLC/(–)ESI-TOFMS technique for a typical yield experiment are listed in Table 2. The error between the measured mass and theoretical mass is reported in two different ways, ppm and mDa. Overall, the error between the measured and theoretical masses is found to be less than ± 2 mDa and ± 5 ppm, allowing for generally unambiguous identification of molecular formulae. None of the listed ions is observed in solvent blanks and control filters. By combining the elemental SOA composition (i.e. TOFMS suggested ion formula) data and the gas-phase data from CIMS, structures for each of the SOA components are also proposed. As shown in Table 2, the types of compounds formed included nitroxy-organic acids, hydroxynitrates, nitroxy-organic peroxides (e.g. nitroxyhydroperoxides), and nitroxy-organosulfates. It should be noted that the data presented in Table 2 are also applicable to all other types of experiments conducted in this study; however, none of the organosulfates are observed in the nucleation experiments, consistent with previous work (Liggio et al., 2005; Liggio et al., 2006; Surratt et al., 2007ab; Iinuma et al., 2007ab). Surprisingly, previously characterized organosulfates of the 2-methyltetrols and the 2-methyltetrol mono-nitrates detected at m/z 215 and m/z 260 (not listed in Table 2), respectively, which are produced from the pho-

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tooxidation of isoprene in the presence of acidified sulfate seed aerosol (Surratt et al., 2007ab; Gómez-González et al., 2007), are also observed in the acid seed experiment shown in Fig. 10, suggesting that nighttime oxidation of isoprene in the presence of acidic seed may also be a viable pathway for these known ambient tracer compounds.

5 Owing to the implementation of reverse-phase chromatography, the SOA components that are more hydrophilic elute from the column the earliest, while the more hydrophobic components elute the latest. It is clear from Table 2 that compounds with the same carbon number and general functionality (i.e. carboxylic acid, alcohol, or organosulfate), but differing number of nitroxy groups, exhibit distinctly different chromatographic behaviors. The presence of more nitroxy groups appears to increase the retention time of the SOA compound. For example, it is found that m/z 194 organic acid compound ($C_5H_8NO_7^-$) containing one nitroxy group elutes earlier than that of the m/z 239 organic acid compounds ($C_5H_7N_2O_9^-$) containing two nitroxy groups. Similarly, the m/z 305 organosulfate ($C_5H_9N_2O_{11}S^-$) elutes earlier than that of the m/z 349 organosulfate ($C_5H_8N_3O_{13}S^-$).

15 SOA components that are either nitroxy-organic acids or nitroxy-organosulfates are detected strongly as the $[M-H]^-$ ion, consistent with previous work (Surratt et al., 2006, 2007ab; Gao et al., 2004ab, 2006), whereas the hydroxynitrates and nitroxy-hydroxyperoxides are detected as both the $[M-H]^-$ and $[M-H+C_2H_4O_2]^-$ ions, with the latter acetic acid adduct ion, in most cases, being the base peak ion (i.e. dominant ion). The acetic acid adduct ions for the hydroxynitrates and the nitroxy-hydroxyperoxides are formed owing to the presence of acetic acid in the UPLC mobile phase. Previous studies have shown that non-acidic hydroxylated species (such as the 2-methyltetrols) and organic peroxides formed from the photooxidation of isoprene (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006) are either undetectable or yield weak negative ions when using (-)ESI-MS techniques. However, it appears that the co-presence of nitroxy groups in the hydroxylated SOA components allow for these compounds to become acidic enough to be detected by the UPLC/(-)ESI-TOFMS technique, or allow for adduction with acetic acid. Further confirmation for the presence of organic perox-

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ides in the isoprene SOA produced from NO_3 oxidation is provided by the iodometric-spectroscopic measurements shown in Table 3. Based upon the UPLC/(-)ESI-TOFMS measurements shown in Table 2, an average molecular weight of 433 for the organic peroxides is assumed for the calculations shown in Table 3. The contribution of organic peroxides to the SOA mass concentration is found to be fairly reproducible for duplicate typical experiments (i.e. 8/22/07 and 10/24/07). The amount of organic peroxides in the excess isoprene experiment is below detection limits.

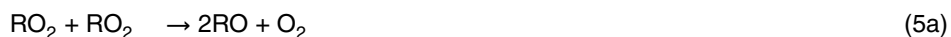
4 Gas-phase chemistry and SOA formation

4.1 Formation of various gas-phase products

10 As seen from Fig. 5 and Fig. 6, the three major first-generation products formed from isoprene- NO_3 reaction are the m/z 230, 232, and 248 ions. Since the CIMS technique uses CF_3O^- (anionic mass 85 Da) as the reagent ion, compounds are detected at a m/z value of their molecular weight (MW) plus 85. The product ions at m/z 230, 232, and 248 likely correspond to C_5 -nitroxy carbonyl (MW 145), C_5 -hydroxynitrate (MW 147), and C_5 -nitroxyhydroperoxide (MW 163). These products have been observed in previous studies (Jay and Stieglitz, 1989; Skov et al., 1992; Kwok et al., 1996; Berndt and Böge, 1997) and their formation from the isoprene- NO_3 reaction is relatively straightforward (Fig. 11). The reaction proceeds by NO_3 addition to the C=C double bond, forming four possible nitroxyalkyl radicals depending the position of the NO_3 attack. Previous studies suggest that NO_3 radicals predominantly attack isoprene in the 1-position, with a branching ratio (C1-position/C4-position) varying between 3.5 and 7.4 (Skov et al., 1992; Berndt and Böge, 1997; Suh et al., 2001). In Fig. 11, only the nitroxyalkyl radical formed from the C1 attack is shown. The nitroxyalkyl radicals then react with O_2 to form RO_2 radicals, which react further with HO_2 , RO_2 , or NO_3 radicals under the experimental conditions in this study. The reaction of RO_2 radicals and HO_2 radicals leads to the formation of C_5 -nitroxyhydroperoxide (m/z 248). The

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reaction of two RO₂ radicals (self reaction or cross reaction) has three different possible channels:



The second channel results in the formation of C₅-nitroxycarbonyl (*m/z* 230) and C₅-hydroxynitrate (*m/z* 232). According to channel (5b), these two products should be formed with a 1:1 ratio; however, C₅-nitroxycarbonyl can also be formed from alkoxy radicals (either from RO₂+RO₂ reaction or RO₂+NO₃ reaction). In Fig. 6, about 53 ppb of C₅-nitroxycarbonyl and 25 ppb of C₅-hydroxynitrate are formed after the addition of the first pulse of N₂O₅, indicating ~28 ppb of C₅-nitroxycarbonyl is formed from the fragmentation of alkoxy radicals. The branching ratios for the reaction of small peroxy radicals have been investigated in previous studies. It is found that the branching ratio for channel (5a) for methylperoxy and ethylperoxy radicals is ~0.3–0.4 and ~0.6, respectively (Lightfoot et al., 1992; Wallington et al., 1992; Tyndall et al., 1998). It is likely that the isoprene peroxy radicals react via this pathway to form alkoxy radicals and contribute to the “extra” 28 ppb of C₅-nitroxycarbonyl. Although the concentrations of the product ions measured by CIMS are only rough estimates, the above observation is indicative that most RO₂ radicals react with other RO₂ radicals instead with NO₃ or HO₂ radicals.

Other than C₅-nitroxycarbonyl, C₅-hydroxynitrate, and C₅-nitroxyhydroperoxide, three other minor products (*m/z* 185, 377 and 393 ions) are also observed as intermediate products. The proposed mechanisms for the formation of these gas-phase products are also shown in Fig. 11. Although channel (5c) in the RO₂+RO₂ reaction is found to be minor for small peroxy radicals such as methylperoxy and ethylperoxy radicals (Kan et al., 1980; Niki et al., 1981, 1982; Wallington et al., 1989; Tyndall et

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al., 1998, 2001), the product ion at *m/z* 377 could be the corresponding ROOR product formed from the self reaction of isoprene peroxy radicals. The product ion at *m/z* 185 likely corresponds to the C₅-hydroxycarbonyl. It has been observed in previous studies and it likely arises from the isomerization of nitroxyalkoxy radicals through a 6-member transition state to form a hydroxynitroxy alkyl radical, which then decomposes to form NO₂ and C₅-hydroxycarbonyl (Kwok et al., 1996). Such isomerization has also been proposed to occur in the photooxidation of isoprene (Paulson and Seinfeld, 1992; Carter and Atkinson, 1996; Dibble, 2002). It is possible that the hydroxynitroxy alkyl radical formed proceeds to react with O₂ to form a peroxy radical, which then reacts with the isoprene peroxy radical to form the product ion *m/z* at 393. The product ion at *m/z* 393 shows a slower rate of formation (Fig. 6) compared to other product ions suggesting that it might also be formed from the further oxidation of a first-generation product. 2-methyl-2-vinyl-oxirane has been observed from isoprene-NO₃ reaction in previous studies at 20 mbar in helium (Berndt and Böge, 1997) and 20 Torr in argon (Skov et al., 1994), respectively. When operated in positive mode with H₂O-H⁺ as the reagent ion (products are observed at *m/z*=MW+1), CIMS shows a protonated molecule at *m/z* 85. Although the epoxide yield is found to be <1% of the total reacted isoprene at atmospheric pressure (Skov et al., 1994), the signal at *m/z* 85 can arise in part from the epoxide. The further oxidation of the epoxide results in the formation of an epoxide peroxy radical, which can react with the isoprene peroxy radical to form the peroxide at *m/z* 393. It is noted that a product ion at *m/z* 246 is detected in CIMS, which could arise from the corresponding carbonyl product formed from the reactions of two epoxide peroxy radicals, or from the fragmentation of the epoxide alkoxy radicals. Unlike *m/z* 393, which decays after the addition of the last pulse of N₂O₅, *m/z* 246 stays relatively constant suggesting that it is not being further oxidized by NO₃ radicals. To examine further the possibility of peroxide formation (*m/z* 377 and 393) in the gas phase, an experiment is conducted using 1,3-butadiene as the parent hydrocarbon. The analogous product ions for the 1,3-butadiene system, i.e. *m/z* 349 and 365, are observed in CIMS, providing further indication that the formation of ROOR products

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from two RO₂ radicals is occurring in the gas phase. Further details of the gas-phase chemistry of isoprene and 1,3-butadiene will be forthcoming in a future manuscript.

4.2 Effect of peroxy radical chemistry on SOA yield

The SOA yield ranges from 4.3% to 23.8% for an initial isoprene concentration of 18.4 to 101.6 ppb in the typical yield experiments. While the SOA yield from the slow N₂O₅ injection experiment is roughly the same as that in the typical yield experiments, the SOA yield from the slow isoprene injection experiment is lower (Fig. 3). In both cases, ~40 ppb of isoprene is consumed, the main difference being the relative importance of RO₂+RO₂ reaction versus RO₂+NO₃ reaction in each system. In the slow N₂O₅ injection experiment, a relatively small amount of NO₃ is available in the chamber. Once RO₂ radicals are formed, it is expected that they would react primarily with other RO₂ radicals instead of NO₃ radicals owing to the presence of a relatively higher isoprene concentration in the chamber. On the other hand, the slow isoprene injection experiment favors RO₂+NO₃ reaction owing to the presence of excess N₂O₅ in the chamber. Thus the higher SOA yield observed in the slow N₂O₅ injection experiment suggests the products formed via RO₂+RO₂ reaction partition more readily into the aerosol phase, or the RO₂+RO₂ reaction forms products that further react and contribute significantly to aerosol growth. The fact that the SOA yield from the slow N₂O₅ injection experiment is roughly the same as in the typical yield experiments implies that RO₂+RO₂ reaction dominates in typical yield experiments.

The time profile for the three major first-generation gas phase products and SOA growth from the slow N₂O₅ injection experiment and slow isoprene injection experiment are shown in Fig. 12 and Fig. 13, respectively. In both cases, once the first-generation products are formed they can react further with NO₃ radicals, making it difficult to estimate the formation yields of these products based on the measured concentrations. The extent to which these products react further is expected to be higher in the slow isoprene injection experiment owing to the presence of excess NO₃ in chamber; this is consistent with the relatively lower concentrations of first-generation products ob-

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served. As mentioned before, it is possible that the CIMS signal at the observed *m/z* comprises isomers formed from the NO₃ attack at positions other than the C1 carbon. Such isomers have slightly different structures but they could exhibit a very different reaction rate towards NO₃ radicals. For instance, studies have shown that the reaction rates of NO₃ radicals with unsaturated alcohols and unsaturated carbonyl compounds can vary by several orders of magnitude depending on the position of the substituted methyl group (Noda et al., 2002; Canosa-Mas et al., 2005). It is possible that the minor products formed from NO₃ attack at other positions react much slower with NO₃ radicals, hence the concentrations of the observed product ions do not decay to zero towards the end of the experiment. At the end of the experiment, about 8 ppb and 3 ppb of C₅-hydroxynitrate is left in the slow N₂O₅ injection experiment and slow isoprene injection experiment, respectively. Assuming the amount of reactive isomers and unreactive (or relatively slow reacting) isomers are formed in the same ratio in the slow N₂O₅ injection experiment and the slow isoprene injection experiment, we can deduce that a relatively higher concentration of reactive C₅-hydroxynitrate (as well as the two other first-generation products) is formed in the slow N₂O₅ injection experiment. This is consistent with the larger extent of RO₂+RO₂ reaction (which forms C₅-hydroxynitrate) and the higher SOA yield observed in the slow N₂O₅ injection experiment, as it appears that C₅-hydroxynitrate is an effective SOA precursor (Fig. 6).

4.3 Growth curves: multiple steps in SOA formation

By examining the time-dependent growth curves (organic aerosol, Δ*M*_o as a function of hydrocarbon reacted, ΔHC) we can gain insights into the general mechanisms of SOA formation (Ng et al., 2006, 2007ab). Figure 4 shows the time-dependent growth curves for the slow N₂O₅ injection experiment and the slow isoprene injection experiment, respectively. For the slow N₂O₅ injection experiment, the initial aerosol growth likely arises from the condensation of first-generation products as the presence of excess isoprene in the chamber suppresses their further oxidation. If higher generation products do contribute to SOA formation, they would have to be formed at very rapid

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rates. After isoprene is consumed, aerosol mass continues to increase and results in a “hook” in the growth curve. This indicates that secondary products (or higher generation products) also contribute significantly to SOA formation. The same observation can be made if we examine the reaction profile of a typical yield experiment (Fig. 2):
5 there is further SOA growth after all isoprene is reacted away, indicating that the further oxidation of first generation products are contributing to SOA formed. These observations are consistent with the fact that the decay of first-generation products observed in CIMS (especially the m/z 232 and m/z 377 ions) is strongly anticorrelated with further SOA growth (Fig. 6). On the other hand, the slow isoprene injection experiment does
10 not allow us to differentiate the contribution of first- and second-generation products to SOA formation. With the presence of excess NO_3 radicals in the chamber, the first-generation products formed in the slow isoprene injection experiment would be further oxidized once they are formed. The SOA growth observed throughout this experiment is from the partitioning of these highly oxidized and nonvolatile products. Hence, at
15 the beginning of the experiment, for the same amount of ΔHC , the amount of SOA formed in this experiment is higher than that in the slow N_2O_5 injection experiment, in which the aerosol growth is probably from the condensation of relatively more volatile first-generation products. Both the AMS data and filter sample data (Figs. 8, 9, and 10) show a very similar composition for the final SOA formed in slow N_2O_5 injection experiment and the slow isoprene injection experiment, suggesting a common SOA forming channel. Based on the previous discussion on the effect of peroxy radical chemistry on SOA yields, it is likely that the $\text{RO}_2 + \text{RO}_2$ reaction is the SOA-forming channel in both cases; such a reaction occurs to a large extent in the slow N_2O_5 injection experiments and results in the formation of more SOA.

25 4.4 Proposed mechanisms of SOA formation

The combination of CIMS gas-phase data and elemental SOA composition data provides substantial insights into the mechanisms of SOA formation. Shown in Figs. 14–17 are the proposed SOA formation mechanisms from the further oxidation of the various

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gas-phase products measured by CIMS. The compounds in the boxes are the SOA products detected by UPLC/(–)ESI-TOFMS. Owing to multiple chromatographic peaks observed in the UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) for the negative ions of the proposed SOA products, structural isomers are likely; however, for
5 simplicity we show only one possible isomer for each product formed from a particular reaction pathway. Many of the SOA products detected are formed from the further oxidation of first- or higher-generation products, which is consistent with the observation of continual SOA growth after the complete consumption of isoprene (hence a “hook” in the growth curve). With the large number of nitrate-substituted compounds detected
10 by UPLC/(–)ESI-TOFMS technique, it is also not surprising that AMS shows strong signals at m/z 30 (NO^+) and m/z 46 (NO_2^+).

Shown in Figs. 14 and 15 are the proposed SOA formation pathways from the further oxidation of the m/z 232 (i.e. C_5 -hydroxynitrate) and 377 gas-phase product ions (as detected by CIMS). The decay of these two products has been found to be strongly
15 correlated with aerosol growth (Fig. 6), which is consistent with the large number of SOA products formed from their further oxidation. The further oxidation of these two gas-phase products also yields SOA compounds of the same molecular weight (compounds of MW 371 and 450). Although m/z 393 is a minor gas-phase product, the further oxidation of this compound leads to formation of several SOA products (Fig. 16).
20 As mentioned before, there are two possible formation routes for m/z 393, and the further oxidation of both products is shown in Fig. 16. The further oxidation of the m/z 393 ion appears to yield SOA products that are specific only to this gas-phase product: these include the SOA products of MW 387 and 467.

Figure 17 shows the proposed SOA formation mechanisms from three other gas-phase products (m/z 185, m/z 230, and m/z 277); the further oxidation of these
25 product ions leads to relatively minor SOA products. Although C_5 -nitroxycarbonyl (m/z 230) is the most abundant gas-phase product detected by CIMS, its further oxidation is not well correlated with aerosol growth (Fig. 6). The further oxidation of m/z 230 yields an SOA product at MW 240. This organic acid product is found to be quite mi-

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nor when examining the peak area in its corresponding extracted ion chromatogram (EIC). It is noted that no SOA products are detected from the further oxidation of the C₅-nitroxyhydroperoxide (*m/z* 248) (also a major gas-phase product); it is possible that these hydroperoxide products are not acidic enough to be detected by the UPLC/(–)ESI-TOFMS technique, or degrade during sample workup and/or analysis procedures. It has been shown that hydroxycarbonyl plays a key role in SOA formation from the reaction of linear alkenes with NO₃ radicals (Gong et al., 2005), however, in the isoprene-NO₃ system, the further oxidation of the minor gas-phase product C₅-hydroxycarbonyl (*m/z* 185) leads to the formation of only one minor aerosol product at MW 195. Some evidence for the formation of a C₅-dinitrate first-generation gas-phase product is indicated from the CIMS and UPLC/(–)ESI-TOFMS data. This first-generation gas-phase product has been observed previously by Werner et al. (1997). The CIMS shows a weak signal at *m/z* 277, which could be associated to the dinitrate product; we do not know, however, whether the negative ion efficiently clusters with such compounds. Further evidence for the dinitrate gas-phase product is provided by the UPLC/(–)ESI-TOFMS detection of an SOA product at MW 495, which could result from the further oxidation of a C₅-dinitrate precursor. The precursor compound before the last oxidation step shown in this mechanism in Fig. 17 may exist in the particle phase; however, this compound is not likely to be detected by the UPLC/(–)ESI-TOFMS technique owing to the lack of acidic hydrogens from neighboring hydroxyl and/or carboxyl groups.

The SOA products highlighted in Figs. 14–17 are observed in all major experiments conducted; however, not all of these products are strongly detected in the excess isoprene experiment (Fig. 10c). With the presence of excess isoprene, further oxidations of first-generation products should be minimal and no significant SOA formation is expected. However, SOA growth is observed and it appears from the UPLC/(–)ESI-TOFMS data that enough RO₂+RO₂ chemistry is occurring to yield many of the products shown in Figs. 14–17. When comparing the UPLC/(–)ESI-TOFMS BPCs (Fig. 10) of all experiments, it is clear that the *m/z* 430 and *m/z* 446 are the dominant ions in

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the excess isoprene experiment, while *m/z* 333 is the dominant chromatographic peak in other experiments. The chromatographic peak at *m/z* 430 corresponds to the acetic acid cluster ion for the compound at MW 371, which can be formed from the further oxidation of CIMS *m/z* 232 and 377 ions (Figs. 14 and 15). The chromatographic peak at *m/z* 446 corresponds to the acetic acid cluster ion for the compound at MW 387, which is formed from the further oxidation of CIMS *m/z* 393 (Fig. 16). The detection of these two SOA products (MW 371 and MW 387) suggests that further oxidation of *m/z* 232, 377, and 393 is occurring in the excess isoprene experiment and contributing to SOA growth. It is also possible that CIMS *m/z* 393 (a first-generation product according to one of the formation routes) is nonvolatile enough that it partitions into the aerosol phase and its further oxidation proceeds heterogeneously. Chromatographic peaks such as *m/z* 333 (associated with MW 271 compound), 449 (MW 450 compound) and 554 (MW 495 compound) are not as strong in the excess isoprene experiment owing to the fact there is not enough NO₃ in the system to allow for the formation of these highly oxidized compounds.

As discussed earlier, the formation yields of ROOR from the reaction of two peroxy radicals is very low for small peroxy radicals (Kan et al., 1980; Niki et al., 1981, 1982; Wallington et al., 1989; Tyndall et al., 1998, 2001). However, according to both gas-phase and aerosol-phase data in this study, it appears that RO₂+RO₂ reaction (self reaction or cross-reaction) in the gas phase yielding ROOR products is a dominant SOA formation pathway. Such reaction has been proposed to form low-volatility diacyl peroxides in the SOA formed from cyclohexene ozonolysis (Ziemann, 2002). In the case of self-reaction of peroxy radicals, the molecular weight of the product is essentially doubled, providing an efficient way to form products of low volatility. Owing to the lack of authentic standards, we cannot accurately quantify how much each of the peroxide products contributes to the SOA mass. Nevertheless, the total peroxide measurement (Table 3) indicates that they contribute significantly to the total SOA formed.

From the UPLC/(–)ESI-TOFMS (Table 2) and PILS/IC measurements, it appears that organic acids are not a major contributor to SOA formation from the oxidation of iso-

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prene by NO_3 radicals. The UPLC/(-)ESI-TOFMS technique detects only two minor organic acids at MW 195 and 240. Additionally, the PILS/IC technique does not detect large quantities of any small organic acids. The sum of formate, acetate, glycolate, lactate, oxalate, and pyruvate are usually between $0.01\text{--}0.50\ \mu\text{g m}^{-3}$. These observations are different from the SOA produced in the photooxidation of isoprene (under high- and low- NO_x conditions), in which a large number of organic acids, such as 2-methylglyceric, formic, and acetic acid, are observed (Surratt et al., 2006; Szmigielski et al., 2007). In the photooxidation experiments, the level of organic acids detected under low- NO_x conditions is lower than under high- NO_x conditions. The low- NO_x isoprene SOA was previously found to also have a significant amount of organic peroxides, as detected in the current study (Table 3); however, organic peroxides detected previously in low- NO_x isoprene SOA were not structurally elucidated through MS techniques performed in the present study (Table 2, Figs. 14–17), possibly owing to the lack of nitroxy groups which seem to induce acidity and/or increase the adductive abilities of organic peroxides with acetic acid during the ESI-MS analysis. Overall, it appears that the isoprene- NO_3 SOA is much more similar to the previously studied low- NO_x isoprene SOA. More specifically, it appears that both contain a large amount of organic peroxides, organosulfates (if conducted in the presence of sulfate seed aerosol), and neutral hydroxylated compounds, such as the hydroxynitrates observed in Fig. 14 (e.g. MW 226 and 271 products).

5 Approximate estimate of global production of SOA from isoprene + NO_3

The global chemical transport model GEOS-Chem (v. 7-04-11) (<http://www.as.harvard.edu:16080/chemistry/trop/geos/>) is used to estimate, roughly, global SOA formation from the isoprene + NO_3 reaction. The current version of GEOS-Chem treats mechanistically SOA formation from isoprene + OH, monoterpenes and sesquiterpenes, and aromatics; here we will estimate SOA formation from isoprene + NO_3 by using an approximate, uniform SOA yield of 10% (corresponding to $M_o \cong 10\ \mu\text{g m}^{-3}$ in Fig. 3). It is

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noted that this yield is quite uncertain and the importance of peroxy radical self reactions in this study suggest that the SOA yield in the atmosphere will be highly sensitive to the nature of the nighttime peroxy radical chemistry. Here, we seek to obtain only a “back-of-the-envelope” estimate.

Two global isoprene emissions are available in GEOS-Chem: GEIA (Global Emission Inventory Activity) (Guenther et al., 1995) and MEGAN (Model of Emissions and Gases from Nature) (Guenther et al., 2006). Both models require, as input, meteorological data such as temperature to calculate the amount isoprene emitted. For the present estimate, the meteorological fields employed by Wu et al. (2007), generated by the Goddard Institute for Space Studies (GISS) General Circulation Model III, are used. Meteorological conditions correspond approximately to those of year 2000.

Table 4 presents the annual emissions of isoprene as predicted by each of the emission models, together with the amount of isoprene predicted to react via OH, O_3 , and NO_3 , the global burden, and lifetime. We note that there is a significant difference between the annual isoprene emissions predicted by the earlier and newer emission models. Isoprene + OH accounts for 300 to 400 Tg yr^{-1} of isoprene consumption. Henze et al. (2007) predict that annual SOA production from isoprene + OH is about 13 Tg yr^{-1} (based on the MEGAN inventory and GEOS-4 meteorological fields, which are assimilated fields from actual year 2004). Note that SOA production from isoprene + OH, or any other pathway for that matter, is sensitive to the production of SOA from other hydrocarbon precursors since gas-aerosol partitioning depends on the total organic aerosol mass.

If we take as a rough estimate a 10% SOA yield from the isoprene + NO_3 pathway from the results in Table 4, 2 to 3 Tg yr^{-1} of SOA results from isoprene + NO_3 . This rate of production would make SOA from isoprene + NO_3 as significant as that from sesquiterpenes, biogenic alcohols, and aromatics, each of which produces about 2 to 4 Tg yr^{-1} of SOA (Henze et al., 2007). Owing to efficient photodissociation, NO_3 achieves its highest concentrations at night. By contrast, isoprene emissions are assumed to be zero at night in both emission models. Consequently, the isoprene + NO_3

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reaction occurs only at night, involving isoprene that remains unreacted after each daytime period.

We caution that the estimates above are obtained at the crudest level of approximation, in which a globally uniform SOA yield of 10% from isoprene + NO₃ is applied. As we note from Table 4, there is also a substantial difference between predictions of the two available isoprene emission models; the more recent MEGAN model represents an improved level of understanding over the earlier GEIA model. Predictions of SOA formation from the isoprene + NO₃ pathway are, of course, highly dependent on ambient NO₃ radical concentrations. Nitrate radical concentrations predicted in the current simulations vary from about 0.1 ppt in remote regions of South America to 20 ppt or more in the southeastern USA (in August). Future work will address the simulation of SOA formation from isoprene + NO₃ following the microphysical treatment in GEOS-Chem.

6 Implications

We report a series of chamber experiments investigating the formation of secondary organic aerosols from the reaction of isoprene with nitrate radicals. For an initial isoprene concentration of 18.4 to 101.6 ppb, the SOA yield ranges from 4.3% to 23.8% (typical yield experiments). The SOA yield from the slow N₂O₅ injection experiment (RO₂+RO₂ reaction dominates) is much higher than that from the slow isoprene injection experiment (RO₂+NO₃ dominates), implying that RO₂+RO₂ is a more effective channel of forming SOA. The SOA yield from the slow N₂O₅ experiment is roughly the same as that in the typical yield experiments, suggesting that SOA yields obtained in this study likely represent conditions in which peroxy-peroxy radical reactions are favored. Using a uniform SOA yield of 10% (corresponding to M_o ≈ 10 μg m⁻³), ~2 to 3 Tg yr⁻¹ of SOA results from isoprene + NO₃, which is about 1/4 of the amount of SOA estimated to be formed from isoprene + OH (~13 Tg yr⁻¹) (Henze et al., 2007).

The extent to which the results from this study can be applied to conditions in the atmosphere depends on the relative importance of RO₂+RO₂ versus RO₂+NO₃ re-

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actions in the nighttime troposphere. However, the fate of peroxy radicals in the atmosphere is uncertain owing to the large uncertainties in the reaction rate constants and ambient concentration of both RO₂ and NO₃ radicals (Skov et al., 1992; Kirchner and Stockwell, 1996; Bey et al., 2001ab; Vaughan et al., 2006). A modeling study by Kirchner and Stockwell et al. (1996) suggests that RO₂+NO₃ reaction is important at night; for a moderately polluted site, ~77–90% of the total RO₂ at night is predicted to react with NO₃. These results are at odds with the study by Bey et al. (2001ab), which suggests that NO₃ radicals are not involved significantly in the propagation of RO₂ radicals. Currently, only the reaction rate constants for small, relatively simple RO₂ radicals with NO₃ radicals have been reported (e.g. Biggs et al., 1994; Daele et al., 1995; Canosa-Mas et al., 1996; Vaughan et al., 2006) and they are roughly in the range of (1–3) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. With the oxidation of various volatile organic compounds by O₃ and NO₃ under nighttime conditions, it is expected that multi-functional peroxy radicals would be prevalent; the reaction rates of these complex peroxy radicals warrants future study. Furthermore, more field measurements on the concentrations of peroxy radicals and nitrate radicals would also help to constrain the relative importance of RO₂+RO₂ versus RO₂+NO₃ reaction.

In this study, we have shown that the formation of ROOR from the reaction of two peroxy radicals is an effective SOA-forming channel based on gas-phase data and elemental SOA composition data. This reaction has generally been considered as a minor channel and has not been widely studied. If the results from this study can be applied to other systems (i.e. the reaction of NO₃ radicals with other volatile organic compounds), the organic peroxides could possibly be very important SOA components in all systems; they may not have been identified previously owing to the lack of suitable analytical techniques (such as accurate mass measurements from high resolution MS) and clearly more study is needed.

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Table 1. Initial conditions and results for yield experiments.

Date	T (K)	RH (%)	ΔHC (ppb) ^a	ΔM_o ($\mu\text{g}/\text{m}^3$) ^b	SOA Yield (%)
8/9/07	294	5.1	101.6±0.6	68.1±1.1	23.8±0.5
8/10/07	293	4.7	30.2±0.1	11.5±0.4	13.5±0.5
8/11/07	294	5.4	67.1±0.1	39.3±1.2	20.8±0.7
8/12/07	293	6.0	51.7±0.2	26.7±0.6	18.2±0.5
8/13/07	294	5.7	18.4±0.1	2.2±0.2	4.3±0.5
8/14/07	294	5.5	21.8±0.1	4.8±0.4	7.8±0.6
10/4/2007 ^c	293	5.5	39.5±0.1 ^d	7.9±0.3	7.1±0.6
10/25/2007 ^e	294	6.4	42.0±0.1	16.6±0.6	14.1±0.7

^a Stated uncertainties (1σ) are from scatter in isoprene measurements.

^b Stated uncertainties (1σ) are from scatter in isoprene measurements.

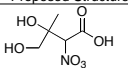
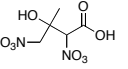
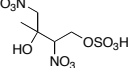
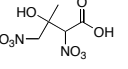
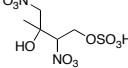
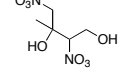
^c Slow isoprene injection experiment

^d Concentration estimated based on a separate calibration experiment (see Sect. 3.2); the uncertainty in the measured isoprene concentration is assumed to be the same as in the slow N_2O_5 experiment.

^e Slow N_2O_5 injection experiment

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Table 2. SOA products identified using UPLC/(–)ESI-TOFMS.

Retention Time (min)	Measured [M – H] [–] Ion (<i>m/z</i>)	TOFMS Suggested		Error (mDa, ppm)	Measured [M – H + C ₂ H ₄ O ₂] [–] Ion (<i>m/z</i>)	TOFMS Suggested		Error (mDa, ppm)	Proposed Structure ^a
		[M – H] [–] Ion Formula	Ion			[M – H + C ₂ H ₄ O ₂] [–] Ion Formula	Ion		
3.68 ^b	194.0310	C ₈ H ₈ NO ₇ [–]		0.9, 4.6	c				
4.52 ^b	239.0137	C ₈ H ₇ N ₂ O ₉ [–]		-1.5, -6.3					
5.09 ^d	304.9946	C ₈ H ₈ N ₂ O ₁₁ S [–]		1.9, 6.2					
5.24 ^b	239.0152	C ₈ H ₇ N ₂ O ₉ [–]		0.0, 0.0					
5.43 ^d	304.9944	C ₈ H ₈ N ₂ O ₁₁ S [–]		1.7, 5.6					
6.07	225.0350	C ₈ H ₈ N ₂ O ₉ [–]		-0.9, -4.0					

3200

Table 2. Continued.

6.12	225.0342	$C_7H_9N_2O_6^-$	-1.7, -7.6				
6.60	225.0375	$C_7H_9N_2O_6^-$	1.6, 7.1	285.0676	$C_7H_{13}N_2O_{10}^-$	0.6, 2.1	
7.75 ^d	349.9775	$C_9H_8N_3O_{13}S^-$	-0.3, -0.9				
7.85 ^d	349.9764	$C_9H_8N_3O_{13}S^-$	0.2, 0.6				
8.00 ^d	349.9784	$C_9H_8N_3O_{13}S^-$	-0.4, -1.1				
8.48 ^d	466.0268	$C_{10}H_{16}N_3O_{16}S^-$	1.7, 3.6				
8.54 ^d	466.0264	$C_{10}H_{16}N_3O_{16}S^-$	1.3, 2.8				

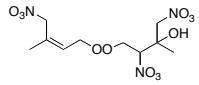
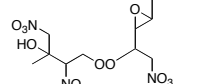
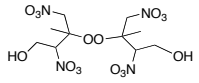
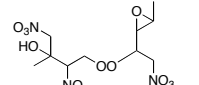
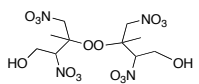
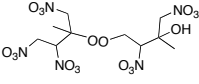
3201

Table 2. Continued.

8.72 ^d	466.0237	$C_{10}H_{16}N_3O_{16}S^-$	-1.4, -3.0				
8.76 ^e	270.0199	$C_7H_9N_3O_{10}^-$	-1.1, -4.1	330.0393	$C_7H_{12}N_3O_{12}^-$	-2.8, -8.5	
8.81 ^d	466.0237	$C_{10}H_{16}N_3O_{16}S^-$	-1.4, -3.0				
8.85 ^e	270.0204	$C_7H_9N_3O_{10}^-$	-0.6, -2.2	330.0379	$C_7H_{12}N_3O_{12}^-$	-4.2, -12.7	
9.15	370.0734	$C_{10}H_{16}N_3O_{12}^-$	0.9, 2.4	430.0940	$C_{12}H_{20}N_3O_{14}^-$	-0.5, -1.2	
9.19	386.0678	$C_{10}H_{16}N_3O_{13}^-$	-0.5, -1.3	446.0888	$C_{12}H_{20}N_3O_{15}^-$	-0.6, -1.3	

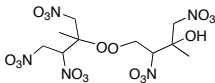
3202

Table 2. Continued.

9.24	370.0732	$C_{10}H_{16}N_3O_{12}^-$	-0.2, -0.5	430.0937	$C_{12}H_{20}N_5O_{14}^-$	-0.8, -1.9	
9.25	386.0683	$C_{10}H_{16}N_3O_{13}^-$	-0.2, -0.5	446.0893	$C_{12}H_{20}N_5O_{15}^-$	-0.1, -0.2	
9.37	449.0637	$C_{10}H_{17}N_4O_{16}^-$	-0.3, -0.7	509.0854	$C_{12}H_{21}N_4O_{18}^-$	0.3, 0.6	
9.41	386.0684	$C_{10}H_{16}N_3O_{13}^-$	0.1, 0.3	446.0903	$C_{12}H_{20}N_5O_{15}^-$	0.9, 2.0	
9.45	449.0653	$C_{10}H_{17}N_4O_{16}^-$	1.3, 2.9	509.0853	$C_{12}H_{21}N_4O_{18}^-$	0.2, 0.4	
9.90 ^f	494.0537	$C_{10}H_{16}N_3O_{18}^-$	4.7, 9.5	554.0669	$C_{12}H_{20}N_5O_{20}^-$	-3.3, -6.0	

3203

Table 2. Continued.

9.98 ^f	494.0518	$C_{10}H_{16}N_3O_{18}^-$	2.8, 5.7	554.0676	$C_{12}H_{20}N_5O_{20}^-$	-2.6, -4.7	
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^a Structural isomers containing nitrate, sulfate, or hydroxyl groups at other positions are likely; for simplicity, only one isomer is shown.

^b These compounds appear to be very minor SOA products due to very small chromatographic peak areas, confirming that the further oxidation of the nitroxy-carbonyl and hydroxycarbonyl first-generation gas-phase products do not yield significant quantities of SOA.

^c A blank cell indicates that the detected SOA product had no observable acetic acid adduct ion (i.e. $[M - H + C_2H_3O_2]^-$).

^d These organosulfate SOA products were observed only in experiments employing either $(NH_4)_2SO_4$ (i.e. neutral) or $MgSO_4 + H_2SO_4$ (i.e. acidic) seed aerosol. These organosulfate SOA products were also observed in the excess isoprene experiments.

^e In addition to the acetic acid adduct ion, these compounds also had a significant adduct ion at $[M - H + HNO_3]^-$ (m/z 333), indicating that these compounds are likely not very stable due to the fragmentation of one of the NO_3 groups during the MS analysis.

^f These compounds were only weakly detected in the excess isoprene experiments.

3204

Table 3. Peroxide content of SOA formed by NO₃ oxidation of isoprene.

Experiment Date	Seeded ^a /Nucleation	[Isoprene] (ppb)	[N ₂ O ₅] (ppm)	SOA Volume Growth	Total SOA Mass	Peroxides Aerosol Mass Concentration	Contribution of Peroxides to the SOA Mass Concentration Observed
				Observed ^b (μg/m ³)	Concentration (μm ³ /cm ³)	(μg/m ³)	(%)
8/22/07	AS	200	1	102	145	46	32
8/30/07	AMS	200	1	123	174	40	23
10/22/07 ^d	AS	1200	0.7	70	100	b.d.l. ^e	f
10/23/07	nucleation	200	1	125	177	31	17
10/24/07	AS	200	1	111	158	47	30
10/27/07 ^g	AS	300	1	110	156	47	30

^a AS=ammonium sulfate seed, AMS=acidified magnesium sulfate seed.

^b Averaged over the course of filter sampling.

^c Assuming a SOA density of 1.42 g/cm³. This was based on DMA and Q-AMS measurements.

^d Excess isoprene experiment.

^e Below detection limits.

^f No observable contribution of organic peroxides to the SOA mass concentration.

^g Slow injection of isoprene in this experiment to enhance the RO₂+NO₃ reaction pathway.

3205

Table 4. Global estimation of isoprene using GEOS-Chem.

	Emission Model	
	GEIA ^a	MEGAN ^b
Isoprene emission (Tg/y)	507	389
Global isoprene burden (Tg)	1.7	1.7
Isoprene lifetime (days)	1.2	1.6
Isoprene reacted (Tg/y) by		
Isoprene + OH	407	304
Isoprene + O ₃	69	62
Isoprene + NO ₃	29	21

^a Modification of GEIA for GEOS-Chem are described at Bey et al. (2001c). Original GEIA reference is Guenther et al. (1995).

^b Guenther et al. (2006).

3206

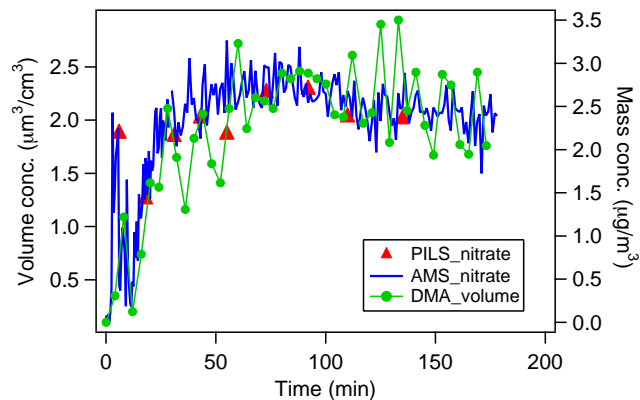


Fig. 1. Time profiles of aerosol volume, inorganic nitrate measured by PILS/IC, and nitrate signals from Q-AMS in a blank experiment (~ 1 ppm N_2O_5 , ammonium sulfate seed, no isoprene).

3207

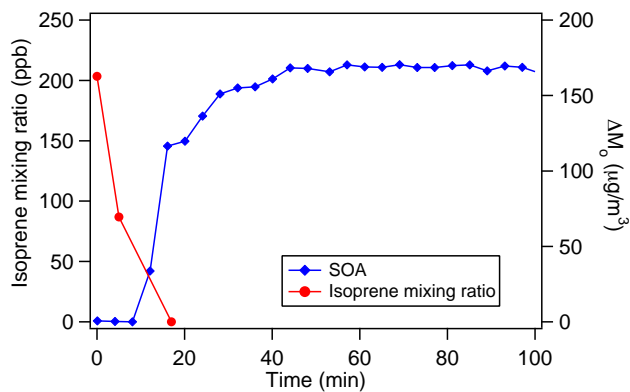


Fig. 2. Reaction profile of the oxidation of an initial mixture containing 203.4 ppb isoprene.

3208

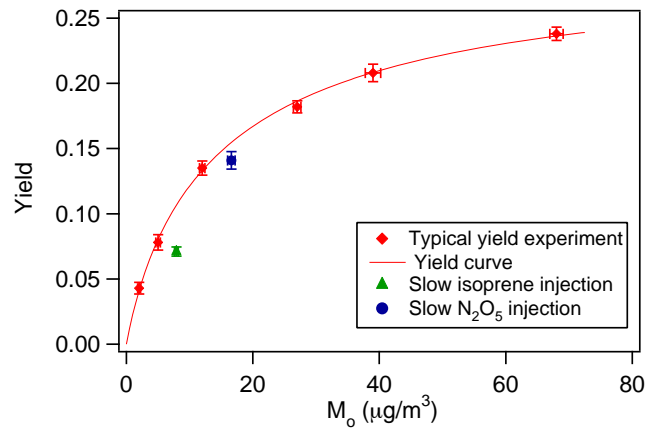


Fig. 3. SOA yield data and yield curve for isoprene- NO_3 reaction. Also shown are SOA yields from the slow N_2O_5 injection experiment and slow isoprene injection experiment.

3209

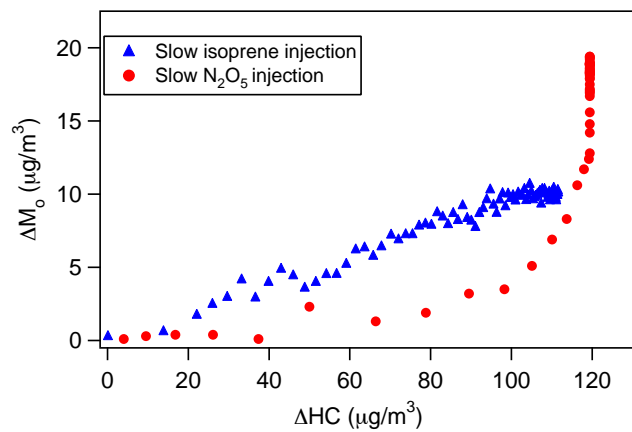


Fig. 4. Time-dependent growth curves for the slow N_2O_5 injection experiment and slow isoprene injection experiment.

3210

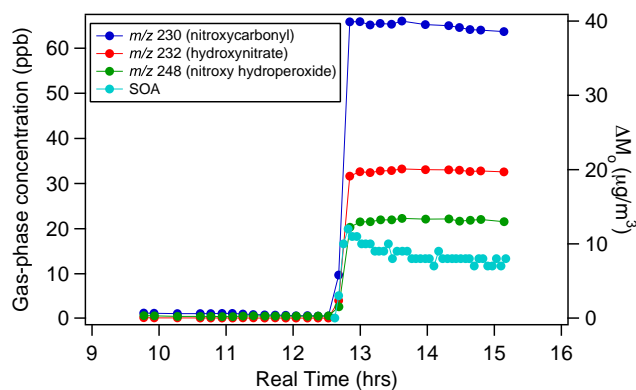


Fig. 5. Time profiles of the major gas-phase products (m/z 230, 232, and 248) and the corresponding aerosol growth from the excess isoprene experiment.

3211

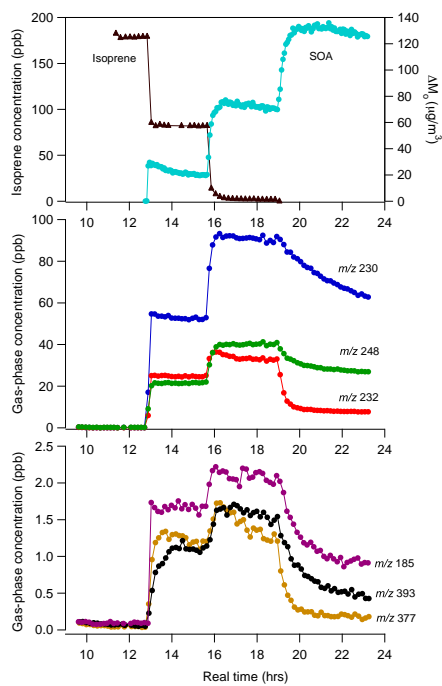


Fig. 6. Time evolutions of various gas-phase products in the staggered N_2O_5 injection experiment (Isoprene is first injected into the chamber, followed by the addition of 3 pulses of N_2O_5 : ~120, 50, and 210 ppb). The top panel shows the isoprene decay and aerosol formation; the middle panel shows the time profiles of the three major first-generation products (m/z 230, 232, and 248); the bottom panel shows the time profiles of three minor products (m/z 377 and 393).

3212

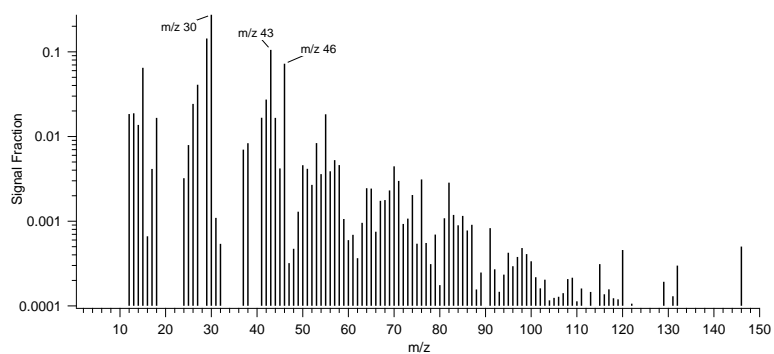


Fig. 7. A typical AMS spectrum for SOA formed in typical yield experiments.

3213

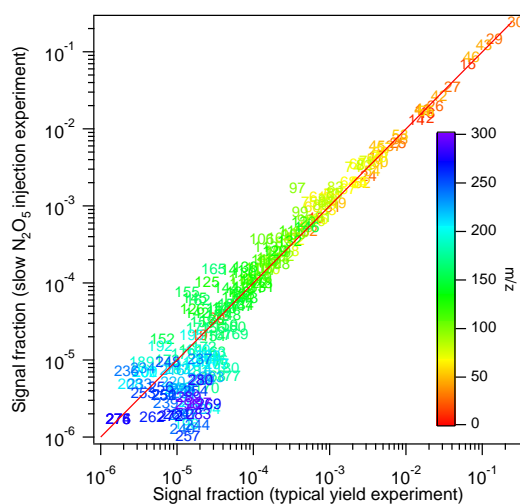


Fig. 8. AMS spectra signal from the slow N₂O₅ injection experiment versus a typical yield experiment. Each mass fragment is normalized by the total signal. The solid red line is the 1:1 line.

3214

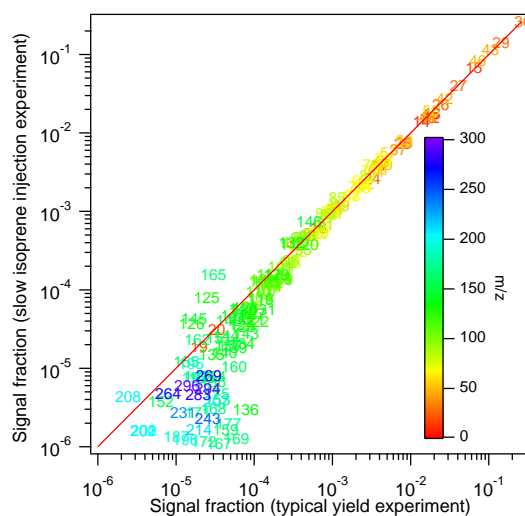


Fig. 9. AMS spectra signal from the slow isoprene injection experiment versus a typical yield experiment. Each mass fragment is normalized by the total signal. The solid red line is the 1:1 line.

3215

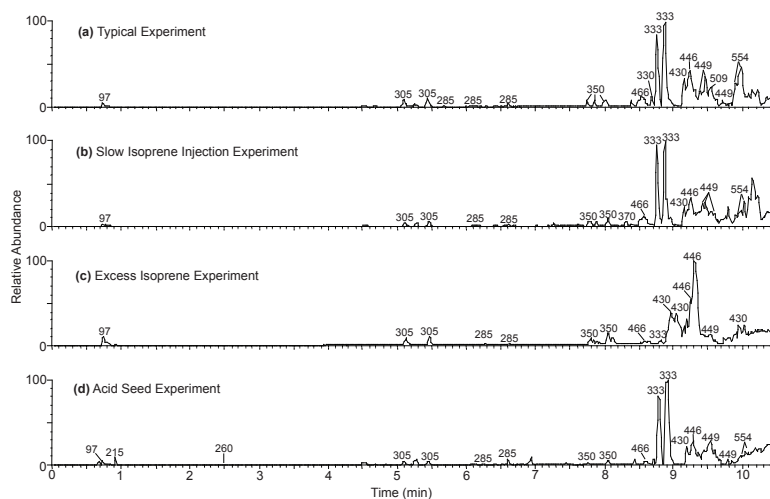


Fig. 10. UPLC/(-)ESI-TOFMS base peak ion chromatograms (BPCs) for the following isoprene- NO_3 oxidation experiments: **(a)** 200 ppb isoprene + 1 ppm N_2O_5 + seed aerosol generated from 15 mM $(\text{NH}_4)_2\text{SO}_4$ atomizing solution; **(b)** 300 ppb isoprene + 1 ppm N_2O_5 + seed aerosol generated from 15 mM $(\text{NH}_4)_2\text{SO}_4$ atomizing solution; **(c)** 1.2 ppm isoprene + 700 ppb N_2O_5 + seed aerosol generated from 15 mM $(\text{NH}_4)_2\text{SO}_4$ atomizing solution; **(d)** 200 ppb isoprene + 1 ppm N_2O_5 + seed aerosol generated from 30 mM MgSO_4 +50 mM H_2SO_4 atomizing solution. The numbers indicated above the selected chromatographic peaks correspond to the most abundant negative ion, and is either the $[\text{M}-\text{H}]^-$ or $[\text{M}-\text{H}+\text{C}_2\text{H}_4\text{O}_2]^-$ ions.

3216

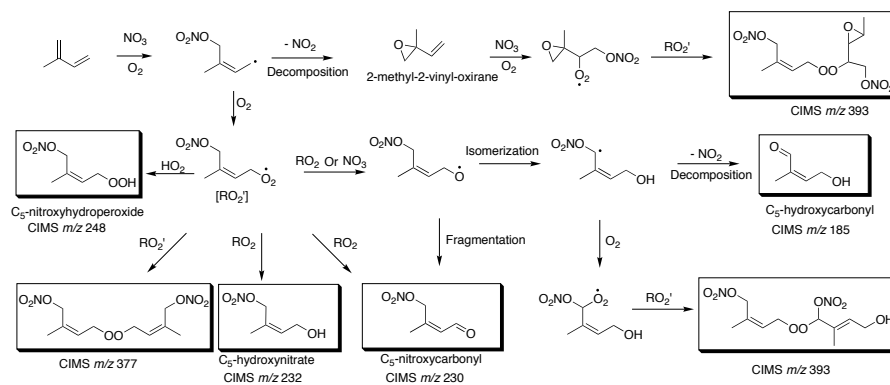


Fig. 11. Proposed mechanisms for the formation of various gas-phase intermediate products observed by CIMS. Multiple structural isomers are possible. In this figure, RO_2' refers to the isoprene peroxy radical (nitroxyperoxy radical), RO_2 refer to a generic peroxy radical.

3217

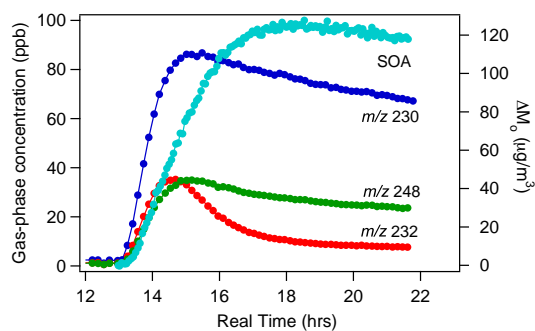


Fig. 12. Time profiles of the major gas-phase products (m/z 230, 232, and 248) and the corresponding aerosol growth from the slow N_2O_5 injection experiment.

3218

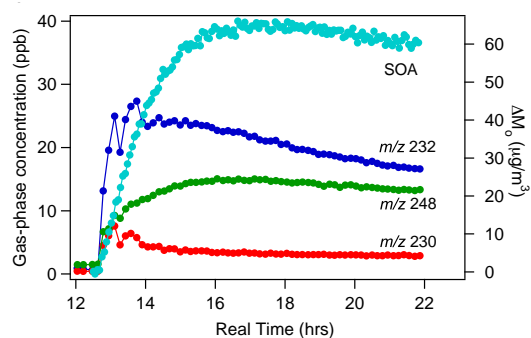


Fig. 13. Time profiles of the major gas-phase products (m/z 230, 232, and 248) and the corresponding aerosol growth from the slow isoprene injection experiment.

3219

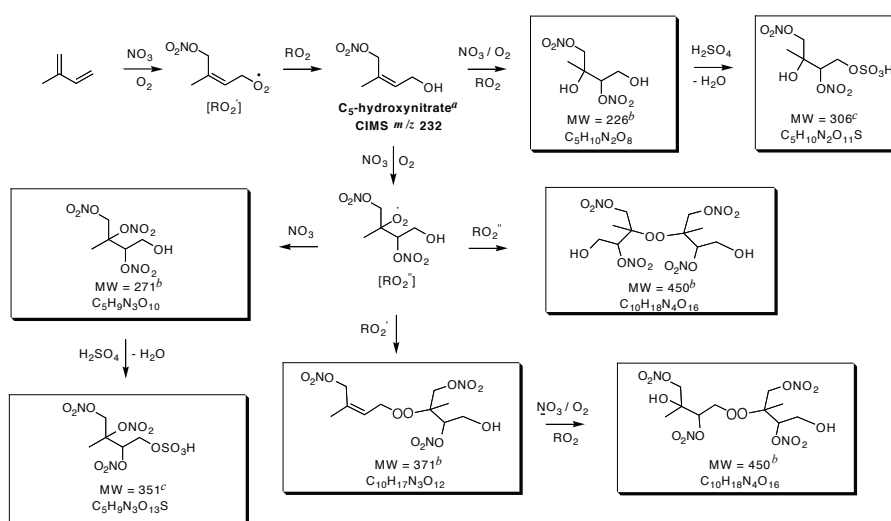


Fig. 14.

3220

Fig. 14. Proposed mechanism for SOA formation from the formation and decay of the C₅-hydroxynitrate gas-phase product formed from the isoprene + NO₃ reaction. Boxes indicate UPLC/(–)ESI-TOFMS detected SOA products; molecular formulas were confirmed by the accurate mass data provided by the UPLC/(–)ESI-TOFMS. Multiple structural isomers are possible, consistent with the multiple chromatographic peaks observed in the extracted ion chromatograms; however, only one structural isomer is shown for simplicity. ^a This first-generation gas-phase product was previously observed by Jay and Stieglitz (1989), Skov et al. (1992), Kwok et al. (1996), and Berndt and Böge (1997); this gas-phase product was detected as the [M+CF₃O][–] ion by the CIMS instrument. ^b These particle-phase compounds were detected as both their [M–H][–] and [M–H+C₂H₄O₂][–] ions; the acetic acid adduct ([M–H+C₂H₄O₂][–]) ion was, in most cases, the molecular ion (i.e. dominant ion). ^c These organosulfate compounds were detected as their [M–H][–] ions and were observed only in ammonium sulfate and acidified magnesium sulfate seeded experiments.

3221

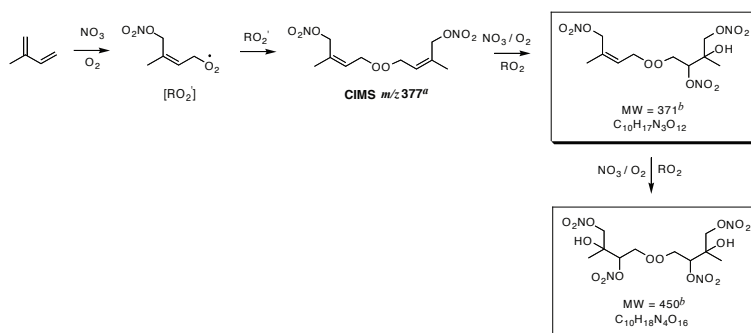


Fig. 15. Proposed mechanism for SOA formation from the formation and decay of the CIMS *m/z* 377 gas-phase product formed from the isoprene + NO₃ reaction. Boxes indicate UPLC/(–)ESI-TOFMS detected SOA products; molecular formulas were confirmed by the accurate mass data provided by the UPLC/(–)ESI-TOFMS. Multiple structural isomers are possible, consistent with the multiple chromatographic peaks observed in the extracted ion chromatograms; however, only one structural isomer is shown for simplicity. ^a This first-generation gas-phase product was detected as the [M+CF₃O][–] ion by the CIMS instrument. ^b These particle-phase compounds were detected as both their [M–H][–] and [M–H+C₂H₄O₂][–] ions; the acetic acid adduct ([M–H+C₂H₄O₂][–]) ion was, in most cases, the molecular ion (i.e. dominant ion).

3222

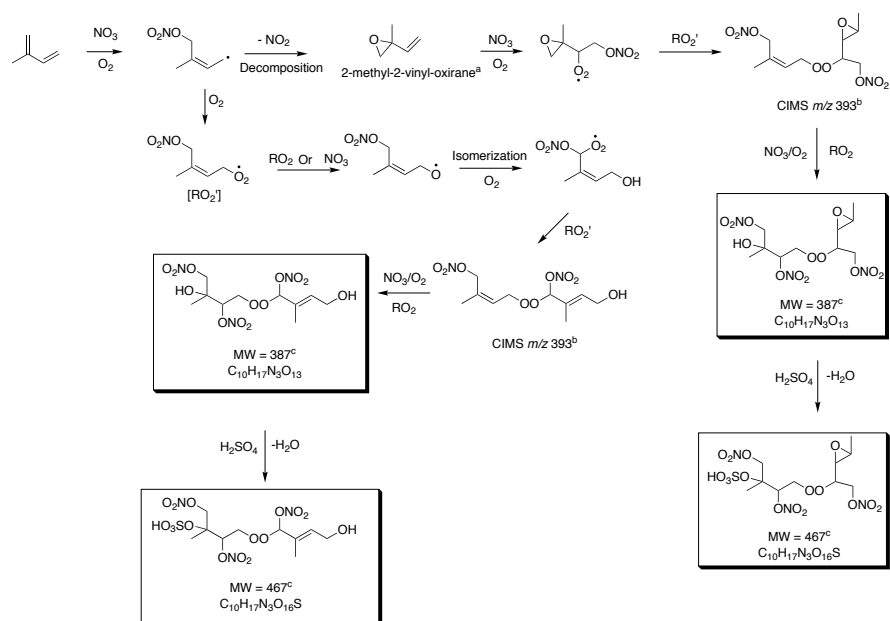


Fig. 16.

3223

Fig. 16. Proposed mechanism for SOA formation from the formation and decay of the CIMS m/z 393 gas-phase product formed from the isoprene + NO_3 reaction. Boxes indicate UPLC/(–)ESI-TOFMS detected SOA products; molecular formulas were confirmed by the accurate mass data provided by the UPLC/(–)ESI-TOFMS. Multiple structural isomers are possible, consistent with the multiple chromatographic peaks observed in the extracted ion chromatograms; however, only one structural isomer is shown for simplicity. ^a This first-generation gas-phase product was detected as the $[\text{M}+\text{H}]^+$ ion by the CIMS instrument; this gas-phase product was previously observed by Berndt and Böge (1997) and could also be 2-(1-methyl-vinyl)oxirane. ^b This gas-phase product was detected as the $[\text{M} + \text{CF}_3\text{O}]^-$ ion. ^c These particle-phase compounds were detected as both their $[\text{M}-\text{H}]^-$ and $[\text{M}-\text{H}+\text{C}_2\text{H}_4\text{O}_2]^-$ ions; the acetic acid adduct ($[\text{M}-\text{H}+\text{C}_2\text{H}_4\text{O}_2]^-$) ion was, in most cases, the molecular ion (i.e. dominant ion). ^d This organosulfate compound was detected as its $[\text{M}-\text{H}]^-$ ion and was observed only in the ammonium sulfate and acidified magnesium sulfate seeded experiments.

3224

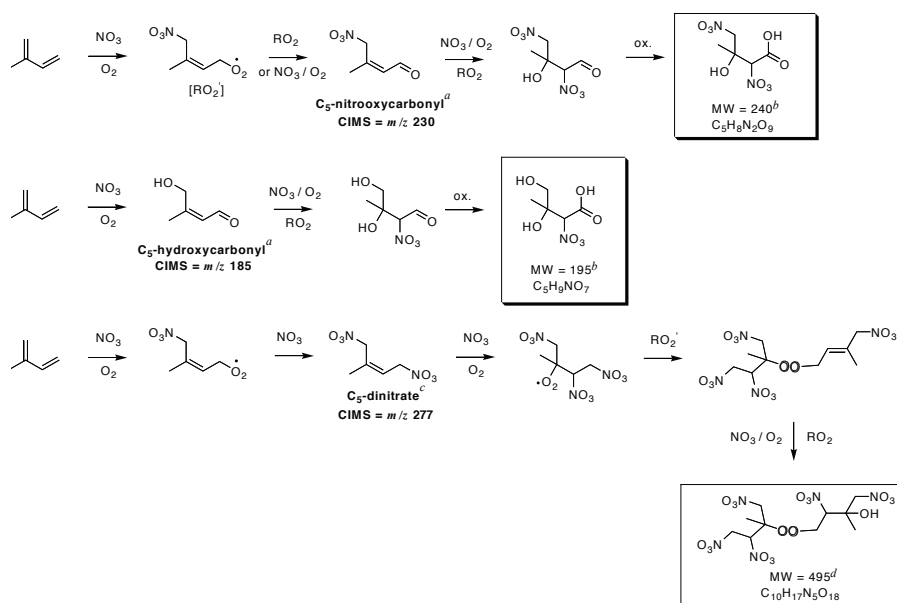


Fig. 17.

3225

Fig. 17. Proposed mechanism for SOA formation from the formation and decay of the C₅-nitrooxycarbonyl, C₅-hydroxycarbonyl, and C₅-dinitrate first-generation products formed from the isoprene + NO₃ reaction. Boxes indicate UPLC/(–)ESI-TOFMS detected SOA products; molecular formulas were confirmed by the accurate mass data provided by the UPLC/(–)ESI-TOFMS. Multiple structural isomers are possible, consistent with the multiple chromatographic peaks observed in the extracted ion chromatograms; however, only one structural isomer is shown for simplicity. ^a These first-generation gas-phase products were previously observed by Skov et al. (1994) and Kwok et al. (1996); these gas-phase products were detected as the [M+CF₃O][–] ion by the CIMS instrument. ^b These are minor SOA products, confirming that the further oxidation of the C₅-nitrooxycarbonyl and C₅-hydroxycarbonyl first-generation products do not yield significant amounts of SOA. ^c This first-generation gas-phase product was previously observed by Werner et al. (1999); this gas-phase product was also detected as the [M + CF₃O][–] ion by the CIMS instrument. ^d This particle-phase compound was detected as both its [M–H][–] and [M–H+C₂H₄O₂][–] ions; the acetic acid adduct ([M–H+C₂H₄O₂][–]) ion was the molecular ion (i.e. dominant ion).

3226