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Observation of isoprene hydroxynitrates in the Southeastern United States and implications for the fate of NO_x

F. Xiong¹, K. M. McAvey¹, K. A. Pratt^{1,3}, C. J. Groff¹, M. A. Hostetler¹, M. A. Lipton¹, T. K. Starn⁴, J. V. Seeley⁵, S. B. Bertman⁶, A. P. Teng⁷, J. D. Crounse⁸, T. B. Nguyen⁸, P. O. Wennberg^{7,8}, P. K. Misztal⁹, A. H. Goldstein^{9,10}, A. B. Guenther¹¹, A. R. Koss^{12,13}, K. F. Olson⁹, J. A. de Gouw^{12,13}, K. Baumann¹⁴, E. S. Edgerton¹⁴, P. A. Feiner¹⁵, L. Zhang¹⁵, D. O. Miller¹⁵, W. H. Brune¹⁵, and P. B. Shepson^{1,2}

 ¹Department of Chemistry, Purdue University, West Lafayette, IN, USA
 ²Department of Earth, Atmospheric and Planetary Sciences, Purdue University, West Lafayette, IN, USA
 ³Department of Chemistry, University of Michigan, Ann Arbor, MI, USA
 ⁴Department of Chemistry, West Chester University of Pennsylvania, West Chester, PA, USA
 ⁵Department of Chemistry, Oakland University, Rochester, MI, USA
 ⁶Department of Chemistry, Western Michigan University, Kalamazoo, MI, USA
 ⁷Division of Engineering and Applied Science, California Institute of Technology, Pasadena,

CA, USA



⁸Division of Geophysical and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

⁹Department of Environmental Science, Policy, & Management, University of California at Berkeley, Berkeley, CA, USA

¹⁰Department of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, CA, USA

¹¹Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, USA

¹²Cooperative Institute for Research in Environmental Sciences, Boulder, CO, USA

¹³NOAA Earth System Research Laboratory, Boulder, CO, USA

¹⁴Atmospheric Research & Analysis, Inc., Cary, NC, USA

¹⁵Department of Meteorology, Pennsylvania State University, University Park, PA, USA

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Correspondence to: P. B. Shepson (pshepson@purdue.edu)

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Abstract

Isoprene hydroxynitrates (IN) are tracers of the photochemical oxidation of isoprene in high NO_x environments. Production and loss of IN have a significant influence on the NO_x cycle and tropospheric O₃ chemistry. To better understand IN chemistry, a series of photochemical reaction chamber experiments were conducted to determine the IN yield from isoprene photooxidation at high NO concentrations (> 100 ppt). By combining experimental data and calculated isomer distributions, a total IN yield of 9(+4/-3) % was derived. The result was applied in a zero-dimensional model to simulate production and loss of ambient IN observed in a temperate forest atmosphere, during the Southern Oxidant and Aerosol Study (SOAS) field campaign, from 27 May to 11 July 2013. By comparing field observations with model simulations, we identified NO as the limiting factor for ambient IN production during SOAS, but vertical mixing at dawn might also contribute (~ 27 %) to IN dynamics. A close examination of isoprene's oxidation products indicates that its oxidation transitioned from a high-NO dominant

chemical regime in the morning into a low-NO dominant regime in the afternoon. A significant amount of IN produced in the morning high NO regime could be oxidized in the low NO regime, and a possible reaction scheme was proposed.

1 Introduction

Isoprene (C₅H₈) accounts for approximately half of the global non-methane biogenic
 volatile organic compound (BVOC) emissions (Guenther et al., 2006) and has a significant influence on the budgets of OH, O₃ and NO_x (Horowitz et al., 2007). Isoprene oxidation by OH in the presence of NO_x can lead to the formation of isoprene hydroxynitrates (IN), as described in Reactions (R1) and (R2). The chain-terminating Reaction (R2a) removes peroxy radicals (RO₂) and NO from the atmosphere and de creases tropospheric O₃ production (Carter and Atkinson, 1996). IN serves as a temporary NO_x reservoir, and the transport and photo-oxidative decomposition of these



compounds can further modulate NO_y and O₃ concentrations (Horowitz et al., 2007; Paulot et al., 2012; Xie et al., 2013). Gas-phase organic nitrates can also partition into the particle phase and undergo hydrolysis, contributing to the growth of secondary organic aerosols (SOA) (Jacobs et al., 2014; Rindelaub et al., 2015).

isoprene + OH(+O₂) \rightarrow RO₂ $RO_2 + NO \rightarrow RONO_2$ (R2a)

$$RO_2 + NO \rightarrow RO + NO_2$$

(R1)

(R2b)

The initial OH addition (followed by O_2) to isoprene (Reaction R1) produces eight isomeric RO₂ radicals. Reaction of these RO₂ radicals with NO proceeds primarily via two reaction pathways (Reaction R2a and b). Laboratory studies suggest that the nitrate formation channel (Reaction R2a) is minor compared to the alkoxy radical (RO) formation channel (Reaction R2b), with reported total IN yields ranging from 4 to 14% (Chen et al., 1998; Patchen et al., 2007; Lockwood et al., 2010; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990). Reaction (R2a) leads to the for-

- mation of eight IN isomers, including four β -IN isomers and four δ -IN isomers (Table 1). 15 The wide range of reported IN yields has led to uncertainty in guantifying isoprene's influence on the NO_x cycle and O₃ enhancement (Xie et al., 2013; Horowitz et al., 2007; Paulot et al., 2012). IN can also be produced at night through NO₃-initiated isoprene oxidation with a yield around 20%, adding to a total organic nitrate yield of 65-70%
- (Rollins et al., 2009; Perring et al., 2009; Kwan et al., 2012). The major daytime IN sink 20 is reaction with OH, which leads to a lifetime of 2.5 to 6.5 h, according to a recent kinetics study (L. Lee et al., 2014). At night, IN is more susceptible to loss from ozonolysis, and potentially NO₃ oxidation when the NO_y concentration is high (Xie et al., 2013). IN have been observed in the ambient environment, primarily in forested areas under the
- influence of anthropogenic NO_x plumes (Grossenbacher et al., 2001, 2004; Giacopelli 25 et al., 2005; Beaver et al., 2012; B. H. Lee et al., 2014). During the BEARPEX 2009 study conducted in the Sierra Nevada Mountains of California, IN constituted 38% of the total organic nitrates (Beaver et al., 2012).



Methods to quantify organic nitrates include infrared spectroscopy (IR), thermal dissociation-laser induced fluorescence (TD-LIF) spectroscopy, chemiluminescence, gas chromatography (GC)-based separation and detection techniques, and mass spectrometry (MS) (Rollins et al., 2010; Tuazon and Atkinson, 1990; Sprengnether et al., ⁵ 2002; Day et al., 2002; O'Brien et al., 1995; Beaver et al., 2012; B. H. Lee et al., 2014; Lockwood et al., 2010; Paulot et al., 2009; Giacopelli et al., 2005; Grossenbacher et al., 2004; Patchen et al., 2007; Hartsell et al., 1994; Kwan et al., 2012; Teng et al., 2015). IR, TD-LIF, and chemiluminescence can only measure total organic nitrates because they respond solely to the nitrooxy functional group (Day et al., 2002; Rollins et al., 2010; Tuazon and Atkinson, 1990; Sprengnether et al., 2002; O'Brien et al., 1995; Hart-10 sell et al., 1994). GC- and MS-based methods can speciate organic nitrates and have been employed previously to quantify IN in both laboratory and field studies (Lockwood et al., 2010; Patchen et al., 2007; Giacopelli et al., 2005; Paulot et al., 2009; B. H. Lee et al., 2014; Grossenbacher et al., 2004; Beaver et al., 2012; Kwan et al., 2012). For MS-based techniques, the fragile O-NO₂ bond in organic nitrates often fragments dur-15

- ing ionization (Perring et al., 2009), so soft-ionization methods with reagent ion such as $H^+(H_2O)_4$, CF_3O^- , and I^- are necessary to detect the molecular ion for organic nitrates (Patchen et al., 2007; Beaver et al., 2012; B. H. Lee et al., 2014; Crounse et al., 2006). Here we present a comprehensive laboratory and field study of the formation of IN
- from isoprene reaction with OH. In the summer of 2013, we quantified ambient IN in rural Alabama for 6 weeks during the Southern Oxidant and Aerosol Studies (SOAS, http://soas2013.rutgers.edu/). In parallel with the field study, laboratory experiments were conducted to determine the yield of IN from isoprene oxidation. For laboratory experiments, we synthesized authentic standards for the quantification of IN, using multi-
- ²⁵ ple calibration techniques. The IN yield obtained from lab experiments was applied in a zero-dimensional model to simulate IN production and loss in the atmosphere, which was then compared with the measurements from SOAS, to examine our understanding of atmospheric IN chemistry.



2 Experiment

2.1 CIMS IN calibration

A chemical ionization mass spectrometer (CIMS) was used to measure IN concentrations during the chamber experiments and the SOAS field study. The instrument is similar to the one described by Lize at al. (2011), which uses $I/(H_{cont})^{-1}$ to form indide

similar to the one described by Liao et al. (2011), which uses $I(H_2O)_n^-$ to form iodide clusters with the analyte compounds.

Two authentic standards, 4,3-IN and 1,4-IN (a mixture of *trans*- and *cis*-1,4-IN), were synthesized to determine the sensitivity of CIMS toward IN isomers. 1,4-IN was prepared using the nitrification method described by L. Lee et al. (2014), and the sample was used after flash column chromatography without further purification to separate the *trans* and *cis* isomers. 4,3-IN was prepared by nitrification of (1-methylethenyl)oxirane, and the epoxide was synthesized following Harwood et al. (1990).

The IN gas-phase sample for CIMS calibration was prepared by evaporating an IN standard solution of known volume into 50 L of clean air. The IN concentration in the standard solution was determined with NMR and FTIR, and the results from the two methods were consistent within 15%. Multiple CIMS calibrations for 4,3-IN were performed, and the results did not deviate more than 15% after 1.5 years (Supplement Sect. 1). The average sensitivity of 4,3-IN normalized to the reagent ion signal was $2.3(\pm 0.3) \times 10^{-3} \text{ ppt}^{-1}$ and was used as the surrogate sensitivity for the β -IN isomers except 1,2-IN.

The 1,4-IN calibration was conducted following the same procedures. Since the 1,4-IN standard contained a mixture of *trans*- and *cis*-1,4-IN, the measured sensitivity was a weighted average of both isomers. The relative abundance of the *trans*- and *cis*-1,4-IN isomers was obtained from NMR, and their individual sensitivities were estimated ²⁵ using a least-squares method (Supplement Sect. 2). The sensitivity for *trans*-1,4-IN was $3(\pm 2) \times 10^{-4}$ ppt⁻¹, and it was used as surrogate sensitivity for *trans*-4,1-IN. The sensitivity for *cis*-1,4-IN was $1.3(\pm 0.3) \times 10^{-3}$ ppt⁻¹, and it was used as surrogate sensitivity for *cis*-4,1-IN.



As we were unable to synthesize the 1,2-IN standard in the condensed phase, a relative method was used, where the CIMS was interfaced with a GC equipped with an electron capture detector (ECD, Fig. 1) to determine the CIMS sensitivity of 1,2-IN relative to 4,3-IN. A mixture of the eight IN isomers was generated by irradiation of a mixture of isoprene, isopropyl nitrite, and NO. The IN mixture was cryo-focused at the head of a 5 m Rtx-1701 column that separated the IN isomers, and the effluent was split into two fused-silica deactivated transfer columns, directed simultaneously to the CIMS and the ECD.

As the CIMS was operated with water addition to the sample gas before ionization, the GC-ECD/CIMS setup enabled direct observation of the influence of water vapor to the sensitivity of the two dominant IN isomers. Figure 2 shows the GC-ECD/CIMS chromatograms with and without water added to the CIMS. The change in retention time was the result of change in initial oven temperature setting, which had little influence on the elution temperature of IN. 1,2-IN and 4,3-IN were the dominant IN isomers

- and 1,2-IN eluted before 4,3-IN, according to a recent study using the same stationary phase (Nguyen et al., 2014b). 1,2-IN and 4,3-IN are expected to have the same ECD sensitivity, because the ECD has similar response to all mono-nitrates and the hydroxyl group in hydroxynitrate has no influence on ECD sensitivity (Hao et al., 1994). Therefore, the CIMS sensitivity of 1,2-IN relative to 4,3-IN was calculated as the ratio of the
- ²⁰ CIMS signal intensity to the corresponding ECD signal intensity, for the pair of isomers. The calculated relative CIMS sensitivity was $0.37(\pm 0.06)$ with water and $0.95(\pm 0.06)$ without water added, determined as the average of three trials for each setup. The result indicated that water addition to the sample air lowered the sensitivity of the 1,2-IN isomer. Hence, 1,2-IN has to be considered separately from the other β -IN isomers²⁵ when calculating the IN calibration factors.

Given the significant difference in sensitivity for different IN isomers, the CIMS IN data have to be interpreted with the knowledge of relative IN isomer distribution, which depends on both IN production and IN loss. Since the IN isomer distribution was not measured in either the laboratory or the field studies, model simulation was used to es-



timate the relative abundance of IN isomers. The distribution of IN isomers during the chamber experiments was estimated using an iterative method (Supplement Sect. 3.1). For IN measurement during SOAS, a diurnal average of the changing IN isomer distribution was estimated and applied to calibrate IN data for each individual day. The isomer-weighted IN sensitivity changed by less than 20 % throughout the day (Supplement Sect. 3.2).

2.2 Isoprene chamber experiments

Seven experiments were conducted in the 5500 L Purdue photochemical reaction chamber (Chen et al., 1998) to determine the yield of IN from OH-initiated isoprene oxidation in the presence of NO_x . OH was generated from the photolysis of isopropyl nitrite. The starting conditions for the experiments are listed in Table 2. Each experiment was initiated by switching on the UV lamps and was considered complete when half of the isoprene was consumed or the NO concentration dropped to around 5 ppb.

The IN concentration was measured continuously during each experiment with the ¹⁵ CIMS. Chamber air was sampled through a 5.2 m long inlet, made of 0.8 cm ID heated (constant 50 °C) FEP Teflon tubing. A total flow of 5 liters per minute (L min⁻¹) was pulled through the inlet into a custom-built three-way valve system (Liao et al., 2011), where 2 L min⁻¹ was sub-sampled into the CIMS through a 0.51 mm orifice. Water vapor was added downstream of the orifice to humidify the sample air to reduce the ²⁰ influence that variations in ambient RH and temperature have on the distribution of $I(H_2O)_n^-$ clusters. Laboratory tests showed that with constant H₂O addition, the CIMS sensitivity is not dependent on ambient air humidity (Supplement Sect. 6). The IN loss in the 50 °C sampling inlet was measured to be 5 % for the 4,3-IN isomer. However,

for the 1,2-IN isomer, it is more susceptible loss under high temperature. This is reflected in the chromatograms in Fig. 2a and b, as the ECD peaks of 1,2-IN and 4,3-IN have approximately the same height, while OH would preferentially add to C1 than C4 (Peeters et al., 2007), leading to a theoretical relative yield of 1.8–2 for 1,2-IN to 4,3-IN. Therefore, it is likely 1,2-IN decomposed in the GC oven with an elution temperature of



80 °C. The loss of 1,2-IN is unclear as it flows through the 50 °C inlet with a residence time of 3s, so an upper limit of 50 % was estimated, based on the loss of 1,2-IN inside the GC system.

Isoprene and its oxidation products, methyl vinyl ketone (MVK) and methacrolein
 (MACR), were quantified with a proton-transfer reaction linear ion trap mass spectrometer (PTR-LIT MS), with measurement precision of 3 ppb and accuracy of ±17% (Mielke et al., 2010). MVK and MACR were observed as the same nominal mass without further differentiation for relative isomeric abundance. The NO concentration was measured through chemiluminescence using the total reactive nitrogen instrument (TRENI) (Lockwood et al., 2010), and the addition of isopropyl nitrite did not cause any interference signal for TRENI during the chamber experiments.

One wall loss experiment was conducted by keeping the IN isomers produced from isoprene oxidation in the dark chamber and sampling the chamber air with CIMS periodically for four hours. No significant IN loss was observed, so wall loss was not corrected for IN measurement.

2.3 CIMS SOAS measurement

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During SOAS, the CIMS was used to measure ambient IN concentrations continuously from 26 May to 11 July 2013 at the Centerville (CTR) site (32.90° N, 87.25° W). The CTR site is located about 50 miles south of Birmingham and Tuscaloosa near the Talladega National Forest, a region abundant with pine and oak trees. The CIMS was operated under the same conditions as those during the chamber experiments. Air was sampled from 5.3 m above the ground, with the same inlet (heated to constant 50°C) and valve system that were used for chamber experiments. The CIMS three-way valve system was used to allow automated background measurement and

 $_{\rm 25}$ in-situ Br₂ calibration to monitor instrument stability. The background was determined by passing ambient air through nylon wool coated with sodium bicarbonate for 2 min every 15 min. Br₂ calibration was performed hourly by adding a 30 sccm Br₂/N₂ flow from a Br₂ permeation device to the ambient air being sampled into the CIMS for 2



min. The CIMS sensitivity to IN was calibrated relative to the Br₂ sensitivity, which were both normalized to the reagent ion signal $I(H_2^{18}O)^-$. The Br₂ output rate from the permeation device was determined daily with the optical absorption method following Liao et al. (2011). The averaged Br₂ output of the permeation source throughout the campaign was $60(\pm 8)$ ng min⁻¹, which was $1.8(\pm 0.2)$ ppb when diluted with ambient air.

2.4 0-D Model for IN data interpretation

A zero-dimensional (0-D) model based on the Master Chemical Mechanism (MCMv3.2) (Jenkin et al., 1997; Saunders et al., 2003) was used to investigate the production and
 loss of IN in the chamber and in the SOAS field study. The mechanism was updated for recent experimental and theoretical studies of isoprene chemistry, including the interconversion of isomeric isoprene RO₂ radicals (LIM1) (Peeters et al., 2014), IN reaction rate constants for OH and O₃ (L. Lee et al., 2014), IEPOX reaction rate constants for OH (Bates et al., 2014) and the branching ratio for NO₃ addition to isoprene (Fan and Zhang, 2004).

For the IN observations during SOAS, our analysis is focused on the production and loss of IN. Therefore, the 0-D model for the SOAS data analysis was constrained to the observed concentrations of the major species involved in the IN chemistry, including isoprene, HO_x , O_3 , NO_x , α -pinene, β -pinene and limonene. The NO₂ photolysis frequency in the 0-D model (J_{NO_2}) was calculated using the Tropospheric Ultraviolet & Visible (TUV) Radiation Model (Madronich and Flocke, 1998) for clear sky conditions with 300 DU ozone, and the model input was scaled relative to observed radiation. The photolysis frequencies for all the other species were scaled relative to J_{NO_2} at zero-degree solar zenith angle.

Because the 0-D model does not take into account the changes in IN concentration as IN was transported to and out of the measurement site both vertically and horizontally, the ratio of total IN concentration to the sum of methyl vinyl ketone (MVK) and



methacrolein (MACR) was used to compare the model results with observations. Major sources of MVK and MACR include isoprene ozonolysis (Grosjean et al., 1993) and OH-initiated isoprene oxidation (Liu et al., 2013). As IN, MVK and MACR are produced simultaneously in the isoprene photochemical oxidation process, the ratio [IN]/([MVK]+[MACR]) may cancel out the influence of dilution caused by vertical mixing and changing boundary layer height, making results from the 0-D model compara-

ble to ambient observations. Besides chemical loss to reaction with OH, O_3 and NO_3 , the model also included loss for dry deposition for IN, MVK and MACR, with averaged daytime deposition velocities of 1.5, 0.7 and 0.4 cm s⁻¹ (Nguyen et al., 2015; Zhang et al., 2002).

Isoprene data from the PTR-ToF-MS measurement were used to constrain the model and its MVK + MACR data were used for model-observation comparison for most days. The MVK and MACR data from the GC-MS measurement were used when knowledge of the relative abundance of MVK and MACR was required to calculate their initial concentrations in the model and when PTR-ToF-MS data were unavailable. The PTR-ToF-

MS data were used primarily because of its higher time resolution. Model constraints on α -pinene, β -pinene and limonene concentrations were based on measurements from GC-MS, and 2D-GC when GC-MS data were unavailable.

3 Results

15

20 3.1 IN yield from chamber experiments

The IN yield was calculated from the production of IN relative to the loss of isoprene, using data obtained in the photochemical reaction chamber experiments. An iterative method was applied to derive a consistent set of total IN yield, IN isomeric distribution and isomer-weighted IN sensitivity (Supplement Sect. 3.1). IN loss by OH oxidation was corrected (Atkinson et al., 1982) with an isomer-weighted rate constant to account for

²⁵ corrected (Atkinson et al., 1982) with an isomer-weighted rate constant to account for the difference in OH reactivity for different isomers (L. Lee et al., 2014). The correction



factor was around 25 % by the end of each experiment. Figure 3 shows the results from the IN yield chamber experiments. The average IN yield was 9 %, based on the slope of Δ IN vs. ($-\Delta$ isoprene). We note that the yield has no apparent [NO] dependence with [NO] varying in the range from 125 to 2400 ppb.

- The relative measurement uncertainties were 15% for IN and 17% for isoprene, based on the instrument calibrations. Uncertainty in the reported rate constants for IN oxidation could cause 20% error when IN data was corrected for OH consumption. The uncertainty in the IN isomer distribution derived from the LIM1 mechanism was 20%, estimated based on sensitivity tests (Supplement Sect. 5). Therefore, the overall relative uncertainty based on error propagation for our experimentally-derived IN yield
- relative uncertainty based on error propagation for our experimentally-derived IN yield is 36 %. When uncertainties in the inlet loss for the 1,2-IN isomer was taken into consideration, a maximum total yield of 12.6 % was derived, based on the assumed limit of 50 % 1,2-IN loss. Therefore, we report our total IN yield to be 9(+4/-3) %, with the asymmetric uncertainty to account for possible underestimated losses. This result lies
- ¹⁵ in the 4–14 % range of IN yields determined from previous experiments (Chen et al., 1998; Patchen et al., 2007; Lockwood et al., 2010; Paulot et al., 2009; Sprengnether et al., 2002; Tuazon and Atkinson, 1990), but is more consistent with determinations from the higher end of the range. Previous IN studies conducted in our group using GC methods consistently resulted in lower IN yields (Chen et al., 1998; Lockwood et al., 1998; Lockwood et al., 1998; Chen et al., 1998; Lockwood et al., 1998;
- 20 2010). We partially attribute the discrepancy of our previous and current work to the possible loss of the 1,2-IN isomer in the GC column and metal sample injection system. This work employed MS to quantify IN during the chamber experiments to circumvent these problems. The current yield result will be applied in the 0-D model to simulate IN concentrations during SOAS. The model-measurement agreement offers a metric to evaluate the validity of the laboratory-derived IN yield.

3.2 Observation of IN during SOAS

Figure 4 shows the temporal profile of total IN mixing ratio observed during the SOAS field study with an averaging 10 min time resolution. In general, fast IN production was



observed after sunrise. On average, the concentration rose to peak around 70 ppt at 10:00 a.m. (Fig. 5) and then decreased to a minimum around 10 ppt by 6:00 a.m. the next day, as a result of vertical mixing, boundary layer expansion, dry deposition and further oxidation. IN concentrations were significantly lower from 04 to 08 July, due to ⁵ wet deposition and less photochemical reactivity caused by continuous rain events.

In contrast to the IN average diurnal profile (Fig. 5), the diurnal profiles for isoprene, OH, and NO_x and MVK + MACR, each peaked at different times of the day (Fig. 6). The decrease in IN, and continued increase of MVK and MACR around 10:00 a.m. can be attributed to the competition among the four RO_2 loss channels (Reactions R2–R5).

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$
(R3)

$$RO_2 + RO_2 \rightarrow 2RO + O_2$$

$$RO_2 \rightarrow products$$

The fraction of RO₂ loss to NO reaction is defined as γ , which is calculated with the following equation.

 $\frac{k_{\text{RO}_2+\text{NO}}[\text{NO}]}{k_{\text{RO}_2+\text{NO}}[\text{NO}] + k_{\text{RO}_2+\text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2+\text{RO}_2}[\text{RO}_2] + k_{\text{isomerize}}}$

Isoprene RO₂ loss to permutation reactions (R4) was calculated assuming $[RO_2] = [HO_2]$, and the rate constant $1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used (Jenkin et al., 1997). Isoprene RO₂ loss rates for reaction with NO and HO₂ (Reactions R2 and R3) were calculated based on observed NO and HO₂ concentrations, using rate constants $k_{\text{RO}_2+\text{NO}} = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{RO}_2+\text{HO}_2} = 1.61 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 20 10^{-11} cm³ molecule⁻¹ s⁻¹ (Saunders et al., 2003; Stevens et al., 1999). The sum of the first-order RO₂ loss rate for reaction with NO, HO₂ and RO₂ was 0.01–0.07 s⁻¹ (Fig. 7a). Therefore, contribution from 1,5-H shift for β -RO₂ was negligible, due to the small isomerization rate constant (Peeters et al., 2014). However, for isoprene cis- δ -RO₂, the 1,6-H shift rate constant is on the order of 0.1–1 s⁻¹ (Peeters et al., 2009, 25

(R4) (R5)

(1)



2014; Crounse et al., 2011). This fast isomerization depletes cis- δ -RO₂ radicals rapidly to form closed-shell products, e.g. hydroperoxy aldehyde (HPALD), and makes the relative abundance of cis- δ -RO₂ radicals very small (~1 %, Supplement Sect. 4). For this reason, $k_{\text{isomerize}}$ was omitted from the calculation of γ , but the yield of total RO₂ was ⁵ incorporated when estimating the production rate of total IN, to account for rapid loss of *cis*- δ -RO₂ to 1,6-H shift.

The calculated diurnal average of the γ value is shown in Fig. 7b. For RO₂ radicals that were lost to reaction with NO or HO₂, the RO₂ + NO reaction was the sole contributor in the early morning, but it was surpassed by $RO_2 + HO_2$ reaction before noon, as the NO concentration decreased steadily throughout the day. The IN production rate was calculated with the following equation.

 $P_{\text{INI}} = k_{\text{ISOP}+\text{OH}}[\text{OH}][\text{ISOP}] \cdot \Phi \cdot \gamma \cdot \alpha$

10

 Φ is the yield of total RO₂ from OH addition to isoprene that are available to react with NO, HO₂ and RO₂, with an RO₂ lifetime in the range of 10–20 s. The calculated Φ is 0.83 (Supplement Sect. 4), with contribution from β -RO₂ being 0.81, *cis*- δ -RO₂ being 15 0.01 and *trans*- δ -RO₂ being 0.02, and the remaining 17 % products from isoprene OH oxidation are closed-shell species such as HPALD. The IN production rate decreased with the declining γ value (Fig. 7b), even though the concentrations of OH and isoprene each peaked at ~1:00 p.m. This could lead to IN loss from OH oxidation to exceed IN production, making IN peak around the time when HO₂ reaction became the major RO₂ 20 loss channel ($\gamma < 0.5$). In this relatively clean environment, MVK and MACR production continued through isoprene ozonolysis (Grosjean et al., 1993) and OH oxidation in the low NO regime (Liu et al., 2013). The MVK + MACR production rate was calculated using the following equation.

²⁵
$$P_{\text{MVK+MACR}} = k_{\text{ISOP+OH}}[\text{OH}][\text{ISOP}] \cdot \Phi_{\beta} \cdot \gamma \cdot (1 - \alpha)$$

+ $k_{\text{ISOP+OH}}$ [OH][ISOP] · Φ · (1 – γ) · 0.06 + $k_{\text{ISOP+O}_2}$ [O₃][ISOP] · 0.61 (3)

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Discussion

Discussion

(2)

 Φ_{β} denotes the yield of isoprene β -RO₂, the precursors for MVK + MACR, and the calculated Φ_{β} was 0.81 (Supplement Sect. 4). The term $k_{\text{ISOP+OH}}[\text{OH}][\text{ISOP}] \cdot \Phi_{\beta} \cdot \gamma \cdot (1 - \alpha)$ is the production rate of MVK + MACR with the isoprene β -RO₂ undergoing the RO₂ + NO reaction pathway. The term $k_{\text{ISOP+OH}}[\text{OH}][\text{ISOP}] \cdot \Phi \cdot (1 - \gamma) \cdot 0.06$ is the production rate of MVK + MACR when the isoprene RO₂ proceeds via HO₂ reaction pathways to form MVK + MACR with an overall yield of 6 % (Liu et al., 2013). The term $k_{\text{ISOP+O}_3}[O_3][\text{ISOP}] \cdot 0.61$ is the production rate of MVK + MACR from isoprene ozonolysis, with a total yield of 61 % (Grosjean et al., 1993).

As shown in Fig. 7b, the production rates of IN and MVK + MACR both plateaued

¹⁰ around 10:00 a.m. For MVK + MACR, the decrease was later compensated with production from the HO₂ and O₃ pathway, and the production rate peaked around 2:00 p.m. when radiation was strong. For IN, however, its production rate did not increase with radiation due the limited availability of NO (small γ value). Therefore, the change in the relative importance of the two RO₂ sinks, RO₂ + NO and RO₂ + HO₂, is likely one of the reasons that IN concentration peaked earlier than MVK + MACR concentration during SOAS.

The early morning increase in IN concentration could imply significant contribution from downward mixing of accumulated IN in the residual layer (RL), as the inversion is broken up after dawn (Hastie et al., 1993). When the earth surface cools in the evening, the remnants of the upper daytime boundary layer are isolated from the lower region near the ground, and the RL forms. The RL contains the same amount of isoprene, IN, and NO_x as is found near the ground around sunset, thus serving as an IN reservoir at might (Naw et al., 1994). While IN in the might increase here a substant of the same and the same a

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- night (Neu et al., 1994). While IN in the nighttime boundary layer (NBL) is slowly lost to dry deposition, IN in the RL, which is isolated from the ground, is better preserved. In
- addition, IN production from reaction of isoprene with NO₃ may also contribute to RL IN, but this process is not as important in the NBL, because NO₃ is likely to be titrated by reaction with NO near ground (Stutz, 2004). As a result, the IN concentration in the RL is expected to be higher than that in the NBL before dawn. During sunrise, IN in the RL can mix downward, which in combination with photochemical IN production leads



to an increase in IN near the ground. The relative importance of these two processes will be assessed with our 0-D model in the following section.

3.3 0-D model for IN photochemistry during SOAS

Due to limited availability of overlapping data for model input from multiple instruments, ambient data for the following 12 days were used: 14 June, 16 June, 22 June, 23 June, 25 June–01 July and 03 July. For each day, only the daytime chemistry (5:00 a.m.– 7:00 p.m.) was simulated, when photochemical reactivity was high. The observed IN and MVK + MACR concentrations at 5:00 a.m. were used as the initial concentrations for modeling. For isoprene, α -pinene, β -pinene, limonene, NO, NO₂, OH, HO₂, and

- ¹⁰ O₃, the model concentrations were constrained to observations for the entire modeling period. The branching ratio for IN formation resulting from the isoprene RO₂ with NO reaction was set to 0.09 for all isomers, which is based on our measured 9% yield from the chamber experiments. As mentioned above, to avoid the complication in the simulation of absolute concentrations caused by transport and changing boundary relayer height we compared the simulated and observed [IN]/([M]/K]+[MACB]) ratio to
- ¹⁵ layer height, we compared the simulated and observed [IN]/([MVK]+[MACR]) ratio to evaluate the model.

Figure 8a shows the temporal profiles of the modeled and observed [IN]/([MVK]+[MACR]) ratio for the selected 12 days. To gain a statistical overview of the model and observation comparison, the 12 day average was calculated (Fig. 8b). The

- ²⁰ 0-D model generally agrees with the observed ratio, lending support to the IN branching ratio determined in the chamber experiments. However, the morning increase was underestimated by the model on certain days (14, 16, 29 June, 01 and 03 July), while on other days (23 and 25–27 June), the decrease rate for the [IN]/([MVK]+[MACR]) ratio was underestimated in the afternoon. Since the IN yield applied in the 0-D model has
- 36 % uncertainty, a sensitivity test on the yield was performed. As shown in Fig. 8c, the simulated [IN]/([MVK]+[MACR]) ratio is highly sensitive to the yield used in the model as expected. The 6 % yield significantly underestimated the ratio in the morning, and the 12 % yield significantly overestimated the ratio in the afternoon.



4 Discussion

4.1 Model-observation comparison for SOAS data

As shown in Fig. 8c, the modeled results deviated from observations from 10:00 a.m. to 12:00 p.m. for the three yields applied, as the simulated [IN]/([MVK]+[MACR]) ratio decreased slowly while the observed ratio dropped rapidly. The fast decrease in the [IN]/([MVK]+[MACR]) ratio implies either fast production of MVK + MACR, or fast consumption of IN. In terms of fast production of MVK + MACR, the formation of MVK + MACR from OH and O₃ have been characterized in the model, and the model was capable of simulating MVK + MACR concentration to within measurement uncertainty for the chamber experiments (Supplement Sect. 3.1). Therefore, the discrepancy between model and observation is more likely associated with underestimated loss rate of IN. The model results with the 6 % yield were lower than observations, despite potential underestimated IN loss rate, so a higher yield (9–12 %) may be more accurate

- to describe the branching ratio for isoprene $RO_2 + NO$ reaction.
- The model overestimation in the afternoon can be caused collectively by measurement uncertainties for model input, uncertainties in the IN loss rates for OH oxidation and deposition, uncertainties in ambient IN and MVK + MACR measurement, and other missing IN loss processes. A recent study found that isoprene hydroperoxide (ISOPOOH) could interfere with MVK and MACR measurement when standard PTR-
- ²⁰ MS and GC methods are used (Rivera-Rios et al., 2014). We found that the model appeared to agree better with observations in the afternoon, if the ISOPOOH + IEPOX concentration was subtracted from MVK + MACR measurement data (Fig. 8d). However, the exact influence of ISOPOOH + IEPOX on the observations of MVK + MACR is unclear, as the ISOPOOH conversion efficiecy is highly dependent on instrumental sampling configuration, and the interferece of IEPOX has not been characterized.

We also considered that an underestimated IN photolysis rate could be one of the reasons for the model-observation discrepancy. The photolysis rate for IN was set to be identical as the photolysis rate for alkyl nitrates in MCMv3.2, but IN isomers have



double bonds and hydroxyl groups, which could increase the IN absorption cross section and enhance the photolytic reactivity for IN. When the IN photolysis rate was increased by 5 times for the 9% yield, or 12.5 times for the 12% yield, the simulated [IN]/([MVK]+[MACR]) ratio was brought closer to observation in the afternoon,

- ⁵ but the IN loss rate still appeared underestimated between 10:00 a.m. and 12:00 p.m. (Fig. 8e). When the higher photolysis rates were applied, the simulated IN loss to photolysis could contribute up to 30% (9% yield case) or 50% (12% yield case) of total IN loss. Since no experimental data were available on the absorption cross spectrum and quantum yield for IN, large photo-dissociation rate coefficients are purely hypothetical.
- ¹⁰ While photolysis may be a significant IN sink in ambient environment, its contribution to IN loss in chamber experiments is negligible, as the lamp radiation was 10% of solar radiation and the durations of the chamber experiments were short. Therefore, no correction for the photolytic loss will be made for the IN measurement performed in chamber experiments.

¹⁵ Despite the discrepancy in absolute values, the simulated [IN]/([MVK]+[MACR]) ratios all peaked in the morning, consistent with observation. The peak signifies the time when the IN loss rate started to exceed the IN production rate. As the OH-loss lifetime of IN decreased from 8:00 a.m. to 1:00 p.m., the IN production rate (Fig. 7b) remained constant during this time. Although isoprene and OH concentrations were both greater after the peoptime, the IN production rate did not increase, due to the small x value.

²⁰ after the noontime, the IN production rate did not increase, due to the small γ value. Therefore, the morning IN peak can be attributed to the combined effects of slow IN production and fast IN consumption in the afternoon, with NO_x being the limiting factor for IN production during this field study.

Although the simulated [IN]/([MVK]+[MACR]) ratios all peaked in the morning, they peaked one hour later than the observed ratio (Fig. 8c). In addition, the modeled ratio had a smaller growth rate than the observed ratio between 7:00 and 9:00 a.m., regardless of the IN yield and IN loss rate applied (Fig. 8c and d). This underprediction implies an unknown source of IN, and we can hypothesize that it was caused by downward mixing of the RL IN, as the fast morning increase of IN coincided with inversion



breakup. By combining the observations of IN and MVK + MACR during SOAS and the results from the 0-D model, we can calculate the growth rate of ambient IN concentration caused solely by isoprene photochemistry in the daytime (Supplement Sect. 7). This photochemical IN growth rate was compared with the observed IN growth rate,

and we estimate that downward mixing can contribute to 27(±16)% of the fast IN increase in the morning, where the large uncertainty originates from the 30% uncertainty in the IN yield.

The residual layer IN concentration before mixing (6:00 a.m.) was estimated with the 0-D model, using the same initial input as the ground-level observation on the previous day at 8:00 p.m. The chemical processes involved are IN production from isoprene oxidation by NO₃ (Reactions R5 and R6b) and IN consumption by OH, O₃ and NO₃. Based on our model calculation, the steady-state NO₃ concentration at night was on the order of 1×10^6 molecules cm⁻³. Nighttime OH was generated through BVOC ozonolysis, and the simulated concentration was on the order of 5×10^4 molecules cm⁻³. Even though the OH concentration was very low at night, it was still the dominant IN loss pathway,

as a result of the fast IN + OH reaction rate constants. It is worth noting that RO_2 produced from isoprene + NO_3 (Reaction R6) also has competing loss channels for reaction with RO_2 (Reaction R7) and with HO_2 (Reaction R8). Therefore, only a fraction of the isoprene nitrooxy peroxy radicals (ONO_2RO_2) can react with other peroxy radicals to produce IN through Reaction (R7b).

 $\begin{array}{ll} C_5H_8 + NO_3(+O_2) \rightarrow ONO_2RO_2 & (R6) \\ ONO_2RO_2 + RO_2 \rightarrow ONO_2RO + RO + O_2 & (R7a) \\ ONO_2RO_2 + RO_2 \rightarrow ONO_2ROH + R'CHO + O_2 & (R7b) \\ ONO_2RO_2 + HO_2 \rightarrow ONO_2ROH & (R8) \end{array}$

Figure 9 shows the simulated IN concentration in the RL and IN observed near ground before dawn, assuming the RL was completely stable at night with no depositional loss for IN from the RL. The simulated IN concentration in the RL before dawn was greater



than the concentrations measured at ground level by up to one order of magnitude, indicating the IN stored in RL overnight may be a significant ground level IN source during inversion breakup. This high IN concentration above the NBL is the result of IN produced during the previous day, which is present with high concentration in the

- ⁵ RL as it is formed, and zero deposition removal overnight. The NO₂ concentration is low when the RL is formed at sunset, so contribution from IN production through NO₃ chemistry is small (1–10 ppt), a minor fraction compared with the concentration of IN already present in the RL in the evening. Isoprene-NO₃ chemistry can generate IN isomers with differently isomeric distribution. Since IN production from this reaction scheme is small, no sensitivity correction was performed to account for the changes in
- isomer distribution when RL IN mixed with ground-level IN in the morning.

The calculated residual layer IN does not take into account the changing IN concentration with altitude caused by OH oxidation, as well as possible IN concentration change cause by advection. Therefore, the actual IN concentration may be very dif-

ferent from the calculated results. This is reflected in a comparison of the large RL IN excess relative to surface IN on 26 and 27 June (Fig. 9) with simultaneous model overprediction of daytime IN on these two days (Fig. 8a). Hence, detailed three-dimensional chemical transport models are needed to fully elucidate the production and storage mechanisms of IN in the ambient environment.

²⁰ 4.2 High-NO_x and low-NO_x chemistry during SOAS

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OH oxidation was the most important daytime sink for BVOCs during SOAS. As the γ value decreased from 0.95 at 7:00 a.m. to 0.3 at 1:00 p.m. (Fig. 7b), the BVOC-derived RO₂ radicals are expected to undergo both NO (high NO_x) and HO₂ (low NO_x) reaction pathways throughout the day. For isoprene, the presence of the two reaction schemes was signified by the oxidation products, with IN peaking in the morning and ISOPOOH and IEPOX peaking in the afternoon (Fig. 10).

As IN was consumed by OH, it would also undertake both NO and HO_2 reaction pathways. Since the highest OH concentrations (1:00 p.m.) were accompanied with



a small γ value (~ 0.3, Fig. 7b), significant amount of IN would be oxidized following the HO₂ pathway. A possible reaction scheme is illustrated in Fig. 11 with 1,2-IN as an example.

Experimental studies by Jacobs et al. (2014) suggest that OH addition to IN can invoke IEPOX formation with a yield of 13 % at atmospheric pressure, which simultaneously releases NO₂. For RO₂ radicals produced from OH addition to IN, 30 % will react with NO and 70 % will react with HO₂ for a γ value of 0.3 at 1:00 p.m.

For the RO₂ + NO reaction, L. Lee et al. (2014) observed the formation of dinitrate for δ isomers of IN and estimated a branching ratio of less than 18% for β -4,3-IN based on missing carbon in the gas phase. The RO radicals from the RO₂ + NO reaction will dissociate to make either MACR nitrate or lose NO₂ to form hydroxyacetone and glycoaldehyde. Both Jacobs et al. (2014) and L. Lee et al. (2014) reported MACR nitrate being the dominant product with an overall yield of 70%, thus making the corresponding branching ratio for the RO radical to be around 80%.

The RO₂ + HO₂ products from IN oxidation are less understood. Alkyl peroxy radical reaction with HO₂ can undergo two reaction channels to afford either hydroperoxide or RO radical and OH. The branching ratio is highly structure dependent. Simple alkyl peroxy radicals, such as CH₃CH₂O₂, can form hydroperoxide with almost unity yield (Hasson et al., 2004). However, for peroxy radicals with *β* carbonyl groups, such as
 RC(O)CH₂O₂, the branching ratio for the OH formation pathway is more than 60 % (Hasson et al., 2004, 2012). The *β* carbonyl oxygen can stabilize the reaction intermediate through internal hydrogen bonding, thus making the reaction favor the formation of OH and RO (Hasson et al., 2005). The RO₂ from IN oxidation has a *β*-OH group and a *β*-NO₃ group, both capable of forming internal hydrogen bonding with the hydrogen of

²⁵ HO₂. Therefore, formation of OH and RO radicals may be a significant reaction channel when the RO₂ radicals derived from IN react with HO₂. The closed-shell product from the RO₂ + HO₂ reaction is dihydroxy hydroperoxy nitrate (DHHPN). This compound has not been identified in any laboratory studies. However, Lee et al. (2015) found a significant amount of compounds with the corresponding molecular formula of C₅H₁₁O₇N



in the aerosol phase during SOAS, which suggests that hydroperoxide formation and aerosol uptake could be an important sink for IN.

A range can be estimated for the NO₂ recycling efficiency for IN oxidation, as the detailed RO₂ + HO₂ reaction mechanism is unclear. If RO₂ + HO₂ reaction forms only ⁵ hydroperoxide, the NO₂ yield from IN oxidation will be 17 %. If RO₂ + HO₂ reaction only undergoes the radical formation channel, the NO₂ yield will be 30 %, and the major products of IN oxidation are highly oxidized secondary nitrates.

5 Summary and atmospheric implications

Our chamber experiments indicate a 9(+4/-3) % nitrate yield from isoprene hydroxyperoxy radical reaction with NO. The product yield provides a more reliable groundwork for future modeling studies on the interplay of isoprene oxidation, NO_x cycling, and tropospheric O₃ production.

Our field measurements and model simulations suggest that in the southeast US, formation of organic nitrates in the boundary layer is controlled by the availability of NO_x. During the SOAS field study, when isoprene was oxidized by OH addition, the NO peak in the morning on average consumed 95% of the isoprene RO₂ to form high NO_x photooxidation products such as IN, MVK and MACR. As the NO_x concentration decreased during the day, the RO₂ + HO₂ reactions became more important, and by ~ 1.00 p.m. only 30% of the RO₂ react with NO, and thus only 2.7% of the RO₂ would form organic nitrates. The high NO_x concentration in the early morning caused an early IN maximum at 10:00 a.m., a combined result of slow afternoon IN production with limited NO_x, and fast IN consumption due to peak radiation and fast OH production in the afternoon. By comparing simulation results with observations, we estimate the inversion breakup after sunrise may contribute to 27(±16)% of the rapid IN increase in the morning. The observed daytime IN loss can be approximated with the current

²⁵ In the morning. The observed daytime IN loss can be approximated with the current understanding of IN oxidation reactions and dry deposition, but some discrepancies



still exist, which could be caused by other less studied loss pathways, such as nitrate photolysis.

While IN were produced and destroyed in the morning through high NO_{χ} chemistry, a major portion of the afternoon IN oxidation process involved low NO_{χ} chemistry, which could yield products such as the highly oxidized hydroperoxide DHHPN. DHHPN is expected to have very low vapor pressure and undergo fast dry deposition and aerosol partitioning, possibly followed by hydrolysis and formation of NO₃⁻ and trihydroxy hydroperoxide. This process removes NO_{χ} from the atmosphere and helps to shift the photochemical processes further toward the low NO_{χ} regime, forming a positive feedback mechanism to reduce the atmospheric NO_{χ} concentration. However, more experimental studies are required to elucidate the detailed mechanism for the RO₂ + HO₂ reactions.

During the past 15 years, NO_x emissions in the southeastern US have decreased by more than 50% (Hidy et al., 2014). As more effort is devoted to controlling anthropogenic emissions, the BVOC oxidation processes will start to shift further toward the

low NO_x regime. Isoprene products resulting from oxidation in the low NO_x condition, such as IEPOX, are more prone to reactive uptake and thus contribute more effectively to the growth of SOA than IN (Xu et al., 2015; Surratt et al., 2010; Nguyen et al., 2014a), indicating potentially higher SOA burdens from isoprene chemistry in the future. The

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- ²⁰ low NO_x photochemistry is often complicated by radical reactions including intramolecular H-shift and autoxidation (So et al., 2014; Peeters et al., 2014; Savee et al., 2015; Crounse et al., 2013), so more theoretical and experimental studies of the fundamental reaction kinetics are needed to unravel the complete BVOC oxidation mechanism. The photochemical reactions that involve both the high NO_x and low NO_x pathways can
- ²⁵ yield new highly-oxidized multi-functional nitrate products. Identification, quantification and study of the chemistry of these organic nitrates is essential to understand the fate of NO_x . As the highly-oxidized compounds, such as DHHPN and dinitrate, tend to partition into the aerosol phase, it will be a challenge for the development of analytical



techniques to investigate their aging process in the particle phase and their role in the NO_x cycle.

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Table 2. Initial conditions	for IN	yield	experiments.
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Expt. number	lsoprene (ppb)	Isopropyl nitrite (ppb)	NO (ppb)	Expt. duration (min)
1	140	180	160	16
2	80	180	130	15
3	70	180	130	12
4	120	180	125	14
5	90	180	220	14
6	75	180	210	12
7	85	180	2400	54

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Figure 1. GC-ECD/CIMS setup for the CIMS sensitivity of 1,2-IN relative to 4,3-IN.





Figure 2. GC-ECD/CIMS chromatogram with water **(a)** and without water **(b)** added to the CIMS. The ECD signal is in black and the CIMS signal is in red.





Figure 3. IN and isoprene data for chamber experiments. An average yield of 9 % was obtained from data of the seven experiments.





Figure 4. IN observed during SOAS.











Figure 6. Diurnal average of OH (**a**, 13 June–03 July), isoprene (**b**, 16 June–11 July), NO_x (**c**, 01 June–15 July) and sum of MVK and MACR (**d**, 16 June–11 July).





Figure 7. (a) Diurnal average of RO_2 loss rates for reaction with NO, HO_2 and RO_2 from 22 June to 07 July. **(b)** Diurnal average of γ value and production rates of IN and MVK + MACR from 22 June to 07 July. For MVK + MACR, production from the three reaction channels are shown in different colors.











Figure 9. Modeled IN in the residual layer and IN observed near ground before dawn the next day. The model includes IN production from isoprene oxidation by NO_3 and IN consumption by reaction with OH, O_3 and NO_3 . The modeled IN may be biased, as concentration change caused by transport is not considered.





Figure 10. Diurnal averages of IN and ISOPOOH+IEPOX from 30 May to 04 July.





Figure 11. Possible oxidation mechanism for 1,2-IN with γ = 0.3.

