Comments "…The iterative method to determine the isomer-specific branching ratios is quite critical to the accuracy of the overall analysis. While I am comfortable with the description of the very careful efforts to understand the sources of calibration errors, the manuscript would be improved with a more extended discussion of this method and the results…"

More description of the iterative method was added to page 11 (lines 307-311) of the revised manuscript. To further clarify the iterative method, we have added more detailed description and a flow chart to the supplement section 3.1.

Comments "…In particular, I am intrigued by Supplement Figure S8, which shows the model-determined isomer-specific branching ratios. While it seems to me that this figure contains very important results, I could not find a reference to this figure in the main manuscript…"

Reference to this figure was added to the revised manuscript page 7 (line 201). Please note Figure S8 is now Figure S9 because we added a new figure to describe the iterative method.

Comments "…In particular, Figure S8 shows that there are only two significant isomers formed (1,2-IN and 4,3-IN), which is quite a different result than that reported by both the CIMSbased (Paulot et al. 2009) and GC-based (Lockwood et al. 2010) previous laboratory studies. The new finding suggests that the OH-initiated oxidation of isoprene is more regiospecific than these previous studies indicated, which is interesting (and simplifying with respect to modeling isoprene oxidation). In particular, both of the previous studies identified the various 1,4- and 4,1-HNI isomer-producing reaction pathways as having minor, yet significant, branching ratios, but Figure S8 indicates that they are very minor products. It would be helpful to explain what part(s) of the analysis are responsible for the difference as compared to the two previous laboratory studies…"

Figure S8, which is now Figure S9 in our revised supplement, shows the results of isomer distribution during the SOAS field study. In comparison, the previous work by Paulot et al. (2009) and Lockwood et al. (2010) are focused on experimental chamber studies.

The difference can be explained from two aspects. First, the isoprene nitrates in the field undergo more oxidation degradation than in the reaction chamber. As the 1,4 and 4,1 nitrate isomers have larger OH and O_3 oxidation rate constants than the 1,2 and 4,3 isomers, the 1,4 and 4,1 nitrate are consumed faster in the field, making their contribution to the total IN pool smaller. The second factor is 1,6-H shift of cis-1,4 and cis-4,1 RO_2 isomers and RO_2 interconversion. During the SOAS field study, the NO concentration is in the range that allows a significant amount of cis-1,4 and cis-4,1 RO_2 to undergo H-shift, which reduces the amount of 1,4- and 4,1- RO_2 available to react with NO and form 1,4- and 4,1-nitrates. In chamber studies, however, NO concentrations are in the range that force all the RO_2 radicals to react with NO, making 1,4- and 4,1-nitrates more important. This is clarified in the revised manuscript on page 14 (lines 387-392).

p. 17851 line 25: I'm not familiar with the scrubbing technique described here. Please provide a reference to the method and indicate what species are being removed.

The method and citation are added to the revised manuscript on page 9 (lines 253-256).

p. 17853 line 3: Since the relative quantity [IN]/([MVK]+[MACR] is the critical quantity being analyzed, it would be helpful to know how much the absolute quantity ([MVK]+[MACR]) varied in the SOAS data being analyzed here, as larger variations in the absolute value would have the potential to cause more uncertainty in the relative value. Additionally, can the absolute variations in [MVK]+[MACR] be qualitatively explained according to expected changes in transport and boundary height?

The [MVK]+[MACR] measurement during SOAS has a 40% measurement uncertainty. This is added to page 18 (line 507) of the revised manuscript.

The absolute diurnal concentrations of MVK+MACR are more consistent with the dynamics of photochemistry, with its peaking concentration at around 1:00 PM when radiation was strong, and [isoprene] is large. The changes in MVK+MACR concentrations are also affected by transport and changing boundary layer height. Since we did not apply three-dimensional transport model in this work, we were unable to quantify the influence of transport and boundary layer height on the absolute MVK+MACR concentrations. However, the relative concentrations of IN to MVK+MACR can provide some insight into the isoprene oxidation chemistry, since these meteorological factors influence all three compounds. We have discussed in more detail the MVK+MACR diurnal profile on page 13 (lines 361-364) of the revised manuscript.

p. 17863 line 4: Is the 13% branching ratio OH + HNI pathway to IEPOX under the low NO conditions a significant source of IEPOX in the afternoon, or does the modeling indicate that ISOPOOH is still the dominant precursor of IEPOX?

During the SOAS study, the 24-hour averaged peak is around 80 ppt for isoprene nitrates and 300 ppt for ISOPOOH. The yield of IEPOX is 13% for isoprene nitrate oxidation and ~ 75% for ISOPOOH oxidation (St. Clair et al., 2015). Therefore, ISOPOOH is still the dominant precursor for IEPOX. This is now discussed in the revised manuscript on page 21 (lines 609-611).

Technical corrections

p. 17848 line 14: What is the solvent used in the IN solutions?

Information on the solvent (C_2Cl_4) is now added on page 5 (line 131).

p. 17851 line 14: change to ". . . , so wall loss correction was not applied to the IN measurements."

We have now re-worded the sentence on page 9 (line 240).

p. 17856 equation 2: the alpha term in this equation should be defined immediately as the nitrate branching ratio.

Description of the alpha term is now added on page 14 (line 399).

p. 17859 line 24: typo: “efficiency”

Typo has been corrected on page 18 (line 514).

p. 17862 line 9: typo: “different”

Typo has been corrected on page 20 (line 584).

Reference

St. Clair, J. M., Rivera, J. C., Crounse, J. D., Knap, H. C., Bates, K. H., Teng, A. P., Jørgensen, S., Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and Products of the Reaction of the First-Generation Isoprene Hydroxy Hydroperoxide (ISOPOOH) with OH, The Journal of Physical Chemistry A, 10.1021/acs.jpca.5b06532, 2015.

The authors present a combination of laboratory and field measurements of isoprene nitrates plus related compounds. They use a 0-D chemical model to interpret the data in terms of constraints on isoprene nitrate formation and fate in the atmosphere. This paper is well written and makes a valuable contribution to our developing understanding of isoprene nitrate chemistry in the atmosphere. It should be published. Comments and suggestions are listed below, and are generally minor.

Thank you.

17857, 25: You could still have some IN production from NO3 + isoprene in the NBL. NO is not so high at night that it would dominate NO3 loss. The ratio of the rate coefficients k(NO3+NO)/k(NO3+isoprene) is about 37. Fig 6 shows that NOx at midnight was around 0.6 ppb, but this is almost all NO2, NO at midnight averaged <10 ppt. On the other hand isoprene was >2ppb at midnight. Based on that, isoprene + NO3 would be 5-6 times faster than NO + NO3 at that time. Would this affect your interpretation of the diurnal IN cycle? Would the CIMS detect any of the NO3 + isoprene nitrates with the daytime products, or no?

The CIMS would detect the hydroxynitrates (IN) from NO3 reaction with isoprene near ground. Our IN raw data during the SOAS study was interpreted with an IN isomer distribution estimated by a 0D model. Within this model, IN production from NO3 chemistry was also included, besides IN formation from the OH + isoprene pathway. Therefore, we have already considered the IN formation form NO3 chemistry in our data analysis. This is clarified on page 16 (lines 456-461) of the revised manuscript.

17848, 15-28. Please discuss why you believe it is reasonable to use the sensitivity for 4,3-IN as a surrogate for all other beta INs (aside from 1,2). And likewise using cis/trans-1,4 for cis/trans-4,1.

The CIMS sensitivities toward alkyl alcohol and alkyl nitrates are both around 5 orders of magnitude smaller than its sensitivity toward the isoprene hydroxynitrates. Hence, it is the combination of the OH group and the nitrate group, as well as their relative positions that has the dominant influence on the CIMS sensitivity, which will affect how the molecule binds with the iodide ion, while the structure of the carbon backbone would have little effect. For the IN isomers, the relative positions of the OH group and the nitrate group are α,β position, trans-α,δ position and cis-α,δ position. We assume the same sensitivity can be applied to isomers within each structural group, namely β-isomers, trans-δ isomers and cis-δ isomers. This assumption is consistent with our observation of identical sensitivity for 1,2-IN and 4,3-IN isomers when water is not added to the CIMS. For the case with water addition to CIMS, the smaller sensitivity of 1,2-IN was caused by the smaller amount of 1,2-IN available for detection, as 1,2-IN is lost inside the instrument, rather than from a fundamental difference in the ionization efficiency of 1,2-IN. Primary nitrates (δ-IN, 3,4-IN, and 2,1-IN) and secondary nitrate (4,3-IN) are not as likely to be affected by water (Hu et al., 2011). We have now clarified these assumptions on page 7 (lines 174-184) of the revised manuscript.

17854, 5. Some significant assumptions had to be made for the instrumental sensitivities for the various IN isomers. Only a couple isomers were actually synthesized and calibrated directly, and the derived sensitivities for those range over a factor of 7. These were then used to estimate the sensitivity for other IN isomers. Given that, I find it hard to believe that the reported 15% uncertainty for IN measurements is even close to realistic.

While the sensitivities of the IN isomers vary greatly, the relative contribution of each isomer to the total pool of IN is well understood from the theoretical work on the formation of isoprene RO_2 and experimental studies that measured MVK and MACR formed simultaneously with IN in isoprene oxidation. The measurement uncertainty for IN comes from 1) the measurement uncertainty for each individual isomer obtained in our calibrations and 2) the uncertainty in the relative abundance of each isoprene nitrate, caused by uncertainty in the kinetics data of the LIM1 mechanism (Peeters et al., 2014). 15% uncertainty is associated with instrument calibration only, and the IN measurement uncertainty is around 23%, with both factors considered. We have provided a more detailed discussion on the estimated IN data uncertainty in supplement section 5 and error propagation is clarified on page 12 (lines 329-339) of the revised manuscript.

17849, 20-25. Do we know that 1,2-IN is the only isomer affected by humidity in this way? If that's not the case would that affect your interpretation of the field data? Likewise (17854, 13) do we know that 1,2 is the only isomer affected by inlet loss?

Hu et al. (2011) suggests that primary and secondary organic nitrates do not undergo hydrolysis under neutral condition, but hydrolysis in neutral pH is efficient for tertiary nitrates. Given the fact that the 1,2-IN is the only tertiary nitrate and the short residence time for the ion-molecule reaction, we do not expect the other nitrates to be affected by humidity. We have discussed the humidity sensitivity of IN isomers on page 7 (lines 184-193) of the revised manuscript.

For inlet loss, we have conducted new experiments and found the inlet loss to be around 5% on average for all the isomers, and our data has been corrected for the 5% inlet loss. This is described on page 8 (line 213) of the revised manuscript.

17851, 16-28. Was the sample stream humidified for the field measurements as it was for the lab data? If not, how do you correct for humidity-dependent losses of the various isomers?

The sample was humidified during the field measurement with the same conditions used in the lab experiments. This information is added on page 9 (line 219) of the revised manuscript.

Fig. 7 is well done. The diurnal trend in gamma shows nicely how the fractional importance of RO2 + NO versus other RO2 sinks varies during the day. It may also be worth pointing out that the calculated IN production rate (Fig 7b) is not as peaked in the morning as the RO2 loss rate to RO2 + NO (Fig 7a) or gamma. And that this is because the RO2 concentrations are still quite low at that time. Right?

Right. When the γ value peaks around 6 AM to 8 AM, the isoprene and OH concentrations are relatively low. Therefore, the nitrate production rate is limited by the availability of RO_2. In the afternoon, while only a fraction of RO_2 will react with NO to form organic nitrates, the total amount of isoprene RO_2 is higher due to higher isoprene and OH concentrations. Therefore, the IN production rate does not have an abrupt decrease in the afternoon as the γ value does. This is further clarified in the revised manuscript on page 14 (lines 407-412).

Fig 8, 17859-17860. You consider the possibility of fast photolysis to explain the day time IN decrease. Could heterogeneous losses / deposition be playing a role?

Aerosol formation may be a small sink for IN, but the C5 hydroxynitrate is unlikely to undergo efficient aerosol uptake (Surratt et al., 2010) due to its small molecular weight. Field observations during SOAS suggest that the isoprene-derived SOA components were associated with IEPOX and more oxidized organic nitrates, not the first-generation hydroxynitrates (Lee et al., 2015; Xu et al., 2015). Therefore, we did not consider aerosol uptake as a major factor for the overestimation of [IN]/([MVK]+[MACR]) ratio in the afternoon. This is discussed on page 22 (lines 663-666) of the revised manuscript.

17849, 1-8. It seems this method could be used as a check on the relative sensitivities for all IN isomers. Is it just that 4,3 and 1,2 are the only ones detected with enough signal for the purpose?

The small abundance of the other isomers makes it more difficult to obtain reliable quantification through this method. Therefore, the sensitivity was obtained by synthesizing a standard. This discussion is added to the revised manuscript on page 6 (line 171-173).

17853, 5. Should say “partially cancel the influence of dilution” or “reduce the influence”. Transport could easily affect MVK+MACR differently than INs, just based on differing lifetimes and concentrations in the residual layer, advected air masses, etc.

The change has been made on the revised manuscript on page 10 (line 289).

17853, 11-18. Need a description or at least a mention and citation for the other measurements used (PTR, GC).

Citation for PTR and GC measurements have been added to the revised manuscript on page 11 (line 295 and line 297).

17854, 13-18. Reported 9% IN yield is “in the 4-14% range of IN yields determined from previous experiments (. . .) but is more consistent with determinations from the higher end of the range”. Actually it seems to be exactly in the middle.

We have made the adjustment on the revised manuscript on page 12 (line 342).

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Observation of Isoprene Hydroxynitrates in the Southeastern United States and Implications for the Fate of NO_x

F. Xiong[1], K. M. McAvey[1], K. A. Pratt[1,3], C. J. Groff[1], M. A. Hostetler[1], M. A. Lipton[1], T. K. Starn[4], J. V. Seeley[5], S. B. Bertman[6], A. P. Teng[7], J. D. Crounse[8], T. B. Nguyen[8], P. O. Wennberg[7,8], P. K. Misztal[9], A. H. Goldstein[9,10], A. B. Guenther[11], A. R. Koss[12,13], K. F. Olson[9], J. A. de Gouw[12,13], K. Baumann[14], E. S. Edgerton[14], P. A. Feiner[15], L. Zhang[15], D. O. Miller[15], W. H. Brune[15] and P. B. Shepson[1,2]

[1] Department of Chemistry, Purdue University, West Lafayette, IN

[2] Department of Earth, Atmospheric and Planetary Sciences, Purdue University, West Lafayette, IN

[3] Department of Chemistry, University of Michigan, Ann Arbor, MI

[4] Department of Chemistry, West Chester University of Pennsylvania, West Chester, PA

[5] Department of Chemistry, Oakland University, Rochester, MI

[6] Department of Chemistry, Western Michigan University, Kalamazoo, MI

[7] Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA

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

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

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

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

[12] Cooperative Institute for Research in Environmental Sciences, Boulder, CO

[13] NOAA Earth System Research Laboratory, Boulder, CO

[14] Atmospheric Research & Analysis, Inc., Cary, NC

[15] Department of Meteorology, Pennsylvania State University, University Park, PA

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

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 O_3 chemistry. To better understand IN chemistry, a series of photochemical reaction chamber experiments was~~ere~~ 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 May 27 to July 11, 2013. The 9% yield was consistent with the observed IN/(MVK+MACR) ratios observed during SOAS. 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 (C_5H_8) 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, O_3 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 (RO_2) and NO from the atmosphere and decreases tropospheric O_3 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_x and O_3 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).

$$\text{isoprene} + OH \; (+ O_2) \rightarrow RO_2 \qquad \text{(R1)}$$

$$RO_2 + NO \rightarrow RONO_2 \qquad \text{(R2a)}$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad \text{(R2b)}$$

The initial OH addition (followed by O_2) to isoprene (Reaction R1) produces eight isomeric RO_2 radicals. Reaction of these RO_2 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 formation of eight IN isomers, including four β-IN isomers and four δ-IN isomers (Table 1). The wide range of reported IN yields has led to uncertainty in quantifying isoprene's influence on the NO_x cycle and O_3 enhancement (Xie et al., 2013; Horowitz et al., 2007; Paulot et al., 2012). Isoprene hydroxynitrates~~N~~ can also be produced at night through NO_3-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 is reaction with OH, which leads to a lifetime of 2.5 to 6.5 hours, according to a recent kinetics study (Lee et al., 2014b). At night, IN is more susceptible to loss from ozonolysis, and potentially NO_3 oxidation when the NO_x 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; Giacopelli et al., 2005; Grossenbacher et al., 2004; Beaver et al., 2012; Lee et al., 2014a). 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., 2002; Day et al., 2002; O'Brien et al., 1995; Beaver et al., 2012; Lee et al., 2014a; 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; Hartsell 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; Lee et al., 2014a; Grossenbacher et al., 2004; Beaver et al., 2012; Kwan et al., 2012). For MS-based techniques, the fragile $O-NO_2$ bond in organic nitrates often fragments during 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; Lee et al., 2014a; 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 multiple 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 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 Lee et al. (2014b), 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/C~~H~~$_2$Cl$_4$ ~~-~~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(±0.3)×10^{-3} 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 using a least-squares method (Supplement Sect. 2). ~~The sensitivity for *trans*-1,4-IN was~~

~~$3(\pm2)\times10^{-4}$ppt^{-1}, and it was used as surrogate sensitivity for *trans*-4,1-IN. The sensitivity for *cis*-1,4-IN was $1.3(\pm0.3)\times10^{-3}$ppt^{-1}, and it was used as surrogate sensitivity for *cis*-4,1-IN.~~ The CIMS sensitivity was $3(\pm2)\times10^{-4}$ppt^{-1} for *trans*-1,4-IN and $1.3(\pm0.3)\times10^{-3}$ppt^{-1} 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, Figure 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~~ 4 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 CIMS signal intensity to the corresponding ECD signal intensity, for the pair of isomers. The calculated relative CIMS sensitivity was 0.37(±0.06) with water and 0.95(±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 CIMS sensitivity ~~of~~ to the 1,2-IN isomer. ~~Hence, 1,2-IN has to be considered separately from the other β-IN isomers when calculating the IN calibration factors.~~The small abundance of the other isomers makes it difficult to obtain reliable quantification through this method. Therefore, the sensitivities for cis- and trans-1,4-IN were obtained with a synthesized standard.

The CIMS sensitivities toward alkyl alcohols and alkyl nitrates are both around 5 orders of magnitude smaller than its sensitivity toward the isoprene hydroxynitrates. Hence, it is the combination of the OH group and the NO_3 group, as well as their relative positions that has the dominant influence on the CIMS sensitivity, which will affect how the molecule binds with the iodide ion, while the structure of the carbon backbone would have little effect. For the IN isomers, the relative positions of the OH group and the nitrate group are α,β position, trans-α,δ position and cis-α,δ position. We assume the same sensitivity can be applied to isomers within each structural group, namely β-isomers, *trans*-δ isomers and *cis*-δ isomers. This assumption is consistent with our observation of identical sensitivity for 1,2-IN and 4,3-IN isomers when water is not added to the CIMS. For the case with water addition to CIMS, the smaller sensitivity of the 1,2-IN was caused by the smaller amount of 1,2-IN available for detection, as 1,2-IN is lost inside the instrument, rather than from a fundamental difference in the ionization efficiency of 1,2-IN. Primary nitrates (δ-IN, 3,4-IN, and 2,1-IN) and secondary nitrates (4,3-IN) are not as likely to be affected by water (Hu et al., 2011). As a result, *cis*-1,4-IN was used as a surrogate for *cis*-4,1-IN, and *trans*-1,4-IN was used a surrogate for *trans*-4,1-IN. For the β-IN isomers, 1,2-IN had to be considered separately due to its loss inside the instrument, but 4,3-IN was used as a surrogate for 3,4- and 2,1-IN isomers. Our assignment of CIMS sensitivities~~y~~ for IN isomers is consistent with reports from Lee et al. (2014a).

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 estimate 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 (Figure S9) 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).

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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 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 (lpm) was pulled through the inlet into a custom-built three-way valve system (Liao et al., 2011), where 2 lpm 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 influence that variations in ambient RH and temperature have on the distribution of $I(H_2O)_n^-$ clusters. Laboratory tests showed that with constant H_2O addition, the CIMS sensitivity is not dependent on ambient air humidity (Supplement Sect. 6). The fractional loss inside the 50 °C sampling inlet was measured to be 5 % for a mixture of the eight IN isomers. ~~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 Figure 2a and 2b, 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 no wall loss correction was ~~not corrected~~applied for IN measurement.

2.3 CIMS SOAS measurement

During SOAS, the CIMS was used to measure ambient IN concentrations continuously from May 26st to July 11th, 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, in terms of voltage setting, gas flow and sample humidification. 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 in-situ Br_2 calibration to monitor instrument stability. The background was determined by passing ambient air through nylon wool coated with sodium bicarbonate for 2 minutes every 15 minutes (Crounse et al., 2006). Laboratory tests suggested that the scrubber ~~could~~ removes isoprene-derived organic nitrates, including hydroxynitrates, carbonyl nitrates and hydroxyperoxy nitrates, and acids such as nitric acid and formic acid. Br_2 calibration was performed hourly by adding a 30 sccm Br_2/N_2 flow from a Br_2 permeation device to the ambient air being sampled into the CIMS for 2 min. The CIMS sensitivity to IN was calibrated relative to the Br_2 sensitivity, which were both normalized to the reagent ion signal $I(H_2{}^{18}O)^-$. The Br_2 output rate from the permeation device was determined daily with the optical absorption method following Liao et al. (2011). The averaged Br_2 output of the permeation source throughout the campaign was 60(±8) ng/min, which was 1.8(±0.2) ppb when diluted with ambient air.

2.4 0D Model for IN Data Interpretation

A zero-dimensional (0D) 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 RO_2 radicals (LIM1) (Peeters et al., 2014), IN reaction rate constants for OH and O_3 (Lee et al., 2014b), IEPOX reaction rate constants for OH (Bates et al., 2014) and the branching ratio for NO_3 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 0D 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 NO_2 photolysis frequency in the 0D model (J_{NO2}) 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_{NO2} at zero-degree solar zenith angle.

Because the 0D 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~~ reduce~~out~~ the influence of dilution caused by vertical mixing and changing boundary layer height, making results from the 0D model comparable 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 1.5cm/s, 0.7cm/s and 0.4cm/s (Nguyen et al., 2015; Zhang et al., 2002).

Isoprene data from the PTR-ToF-MS measurement (Misztal et al., In preparation) 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 (Gilman et al., 2010) 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

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. The isomer-weighted IN sensitivity is expected to change during each experiment, as IN isomers are lost to OH consumption with different reaction rate constants. ~~, An~~ To account for the change in IN isomer distribution during each experiment, an iterative method was applied to derive a self-consistent set of total IN yield, IN isomeric distribution and isomer-weighted IN sensitivity (Supplement 3.1). IN loss by OH oxidation was corrected (Atkinson et al., 1982) with an isomer-weighted rate constant to account for the difference in OH reactivity for different isomers (Lee et al., 2014b). 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 ΔIN vs. (-Δisoprene). We note that the yield has no apparent [NO] dependence with [NO] varying in the range from 125 ppb 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 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.~~

The relative uncertainty for isoprene concentrations is 17% based on instrument calibration. The uncertainty for IN concentrations is ~~derived~~caused by both the uncertainty in the CIMS sensitivity for each IN isomer and the uncertainty in the relative abundance of the IN isomers. Through a sensitivity test on the RO_2 interconversion rate constants of the LIM1 mechanism (Supplement Sect. 5), the IN measurement uncertainty was estimated to be +23%/-20%. The fractional loss for the CIMS inlet was 4(±6)%, making the IN measurement uncertainty to be +24%/-20%. The uncertainty in the reported rate constants for IN oxidation could cause 20 % error when IN data was corrected for OH consumption. Therefore, the overall relative uncertainty in our IN yield is +36%/-33% and we report our total IN yield to be 9(+4/-3)% to encompass all the measurement uncertainties. This result lies in the middle of 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., 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 0D 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-minute time resolution. In general, fast IN production was observed after sunrise. On average, the concentration rose to peak around 70 ppt at 10:00 AM (Figure 5) and then decreased to a minimum around 10 ppt by 6:00 AM the next day, as a result of vertical mixing, boundary layer expansion, dry deposition and further oxidation. IN concentrations were significantly lower from Jul 4 to Jul 8, due to wet deposition and less photochemical reactivity caused by continuous rain events.

In contrast to the IN average diurnal profile (Figure 5), the diurnal profiles for isoprene, OH, and NO_x and MVK+MACR, each peaked at different times of the day (Figure 6). While IN and MVK + MACR are products of the parallel RO_2 + NO Reactions (R2a and b), the diurnal MVK + MACR concentrations are more consistent with the temporal profiles of isoprene, OH and O_3 with peak concentration around 1:00 PM when radiation was strong. The decrease in IN, and continued increase of MVK and MACR around 10:00 AM can be attributed to the competition among the four RO_2 loss channels (R2, R3, R4, and R5).

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

$$RO_2 + RO_2 \rightarrow 2RO + O_2 \qquad (R4)$$

$$RO_2 \rightarrow \text{products} \qquad (R5)$$

The fraction of RO_2 loss to NO reaction is defined as γ, which is calculated with the following equation.

$$\gamma = \frac{k_{RO2+NO}[NO]}{k_{RO2+NO}[NO] + k_{RO2+HO2}[HO_2] + k_{RO2+RO2}[RO_2] + k_{isomerize}} \qquad (1)$$

Isoprene RO_2 loss to permutation reactions R4 was calculated assuming $[RO_2]=[HO_2]$, and the rate constant 1.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1} was used (Jenkin et al., 1997). Isoprene RO_2 loss rates for reaction with NO and HO_2 (R2 and R3) were calculated based on observed NO and HO_2 concentrations, using rate constants $k_{RO2+NO} = 9\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{RO2+HO2} = 1.61\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Saunders et al., 2003; Stevens et al., 1999). The sum of the first-order RO_2 loss rate for reaction with NO, HO_2 and RO_2

was 0.01-0.07 s^{-1} (Figure 7a). Therefore, contribution from 1,5-H shift for β-RO_2 was negligible, due to the small isomerization rate constant (Peeters et al., 2014). However, for isoprene *cis*-δ-RO_2, the 1,6-H shift rate constant is on the order of 0.1-1s^{-1} (Peeters et al., 2009; Crounse et al., 2011; Peeters et al., 2014). This fast isomerization depletes *cis*-δ-RO_2 radicals rapidly to form closed-shell products, e.g. hydroperoxy aldehyde (HPALD), and makes the relative abundance of *cis*-δ-RO_2 radicals very small (~1%, Supplement Sect. 4). For this reason, $k_{isomerize}$ was omitted from the calculation of γ, but the yield of total RO_2 was incorporated when estimating the production rate of total IN, to account for rapid loss of *cis*-δ-RO_2 to 1,6-H shift. In addition, the fast 1,6-H isomerization for *cis*-δ-RO_2 decreased the production rates of δ-IN among the IN isomers. With this smaller production rates and their faster loss rates to OH and O_3 (Lee et al., 2014b), the relative abundance of δ-IN during this field study was much smaller than what have been observed in laboratory studies (Lockwood et al., 2010; Paulot et al., 2009).

The calculated diurnal average of the γ value is shown in Figure 7b. For RO_2 radicals that were lost to reaction with NO or HO_2, the RO_2+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.

$$P_{IN} = k_{ISOP+OH}[OH][ISOP] \bullet \Phi \bullet \gamma \bullet \alpha \qquad (2)$$

α is the branching ratio (=$k_{2a}/(k_{2a} + k_{2b})$) for~~of~~ isoprene RO_2 + NO reaction for nitrate formation. Φ is the yield of total RO_2 from OH addition to isoprene that are available to react with NO, HO_2 and RO_2, with an RO_2 lifetime in the range of 10~20s. The calculated Φ is 0.83 (Supplement Sect. 4), with contribution from β-RO_2 being 0.81, *cis*-δ-RO_2 being 0.01 and *trans*-δ-RO_2 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 (Figure 7b), even though the concentrations of OH and isoprene each peaked at ~1:00 PM.~~

γ value peaked around 6:00 AM to 8:00 AM when the isoprene and OH concentrations were relatively low. During this period, the IN production rate was limited by the

Formatted: Font: (Default) Times New Roman availability of RO_2. In the afternoon, when isoprene RO_2 was more abundant with higher isoprene and OH concentrations, the IN production rate was limited by the availability of NO, and decreased with the declining γ value (Fig. 7b) ~~This could~~ The declining γ value could lead to IN loss from OH oxidation to exceed IN production, making IN peak around the time when HO_2 reaction became the major RO_2 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.

$$\begin{aligned} P_{MVK+MACR} &= k_{ISOP+OH}[OH][ISOP]\bullet\Phi_{\beta}\bullet\gamma\bullet(1-\alpha) \\ &+ k_{ISOP+OH}[OH][ISOP]\bullet\Phi\bullet(1-\gamma)\bullet0.06 \\ &+ k_{ISOP+O3}[O_3][ISOP]\bullet0.61 \qquad (3) \end{aligned}$$

Φ_{β} denotes the yield of isoprene β-RO_2, the precursors for MVK+MACR, and the calculated Φ_{β} was 0.81 (Supplement Sect. 4). The term $k_{ISOP+OH}[OH][ISOP]\bullet\Phi_{\beta}\bullet\gamma\bullet(1-\alpha)$ is the production rate of MVK+MACR with the isoprene β-RO_2 undergoing the RO_2+NO reaction pathway. The term $k_{ISOP+OH}[OH][ISOP]\bullet\Phi\bullet(1-\gamma)\bullet0.06$ is the production rate of MVK+MACR when the isoprene RO_2 proceeds via HO_2+~~and~~ RO_2 reaction pathways to form MVK+MACR with an overall yield of 6% (Liu et al., 2013). The term $k_{ISOP+O3}[O_3][ISOP]\bullet0.61$ is the production rate of MVK+MACR from isoprene ozonolysis, with a total yield of 61% (Grosjean et al., 1993).

As shown in Figure 7b, the production rates of IN and MVK+MACR both plateaued around 10:00 AM. For MVK+MACR, the decrease was later compensated with production from the ~~HO_2~~ ~~R~~HO_2 and O_3 pathway, and the production rate peaked around 2:00 PM 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 RO_2 sinks, RO_2+NO and RO_2+HO_2, is likely one of the reasons that the IN concentration peaked earlier than the 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 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 NO_3 may also contribute to RL IN, but this process is not as important in the NBL, because the NO_3 + NO reaction near the ground makes the NO_3 concentrations smaller~~because NO_3 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. Perhaps more importantly, the relative volume fraction of NBL vs. RL is small (~0.1), and thus surface level nighttime chemistry cannot contribute significantly to the surface IN increase at ~10am. ~~Figure 7 shows that the surface (NBL) IN production rate is very low at night, though non-negligible.~~ 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 0D model in the following section.

It is worth mentioning that the nighttime ground-level IN production from NO_3 + isoprene can afford a different IN isomer distribution, which can influence the isomer-weighted IN sensitivity. However, the 0D model simulation of IN isomer distribution has included IN formation from the NO_3 + isoprene pathway. Therefore, our interpretation of the SOAS IN measurement data has considered the changing IN isomer distribution from both the OH- and the NO_3-initiated IN production near ground.

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3.3 0D 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: Jun 14, Jun 16, Jun 22-Jun 23, Jun 25-Jul 1 and Jul 3. For each day, only the daytime chemistry (5:00 AM - 7:00 PM) was simulated, when photochemical reactivity was high. The observed IN and MVK+MACR concentrations at 5:00 AM were used as the initial concentrations for ~~modeling~~simulations. For isoprene, α-pinene, β-pinene, limonene, NO, NO_2, OH, HO_2, and O_3, the model concentrations were constrained to observations for the entire modeling period. The branching ratio for IN formation resulting from the isoprene RO_2 ~~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 the absolute concentration variability from~~s caused by~~ transport and changing boundary 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 (Figure 8b). The 0D 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 (Jun 14, Jun 16, Jun 29, Jul 1 and Jul 3), while on other days (Jun 23 and Jun 25-Jun 27), the decrease rate for the [IN]/([MVK]+[MACR]) ratio was underestimated in the afternoon. Since the IN yield applied in the 0D model has +36%/-33%~~36%~~ uncertainty, a sensitivity test on the yield was performed. As shown in Figure 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 Figure 8c, the modeled results deviated from observations from 10:00 AM to 12:00 PM for all the three yields applied~~,~~. During this period, ~~as ~~the simulated [IN]/([MVK]+[MACR]) ratio decreased slowly, but~~ 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 O_3 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 3.1). Therefore, the discrepancy between model and observation is ~~more likely~~potentially 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 (25%) and MVK+MACR (40%) 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-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 the MVK+MACR measurement data (Figure 8d). However, the exact influence of ISOPOOH+IEPOX on the observations of MVK+MACR is unclear, as the ISOPOOH conversion efficiency 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~~ to 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, but the IN loss rate still appeared underestimated between 10:00 AM and 12:00 PM (Figure 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. While photolysis may be a significant IN sink in the 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~~was made for the IN measurement performed in chamber experiments.

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 AM to 1:00 PM, the IN production rate (Figure 7b) remained constant during this time. Although isoprene and OH concentrations were both greater 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 (Figure 8c). In addition, the modeled ratio had a smaller growth rate than the observed ratio between 7:00 AM and 9:00 AM, regardless of the IN yield and IN loss rate applied (Figure 8c and 8d). 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 0D 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 from that 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 AM) was estimated with the 0D model, using the same initial input as the ground-level observation on the previous day at 8:00 PM. The chemical processes involved are IN production from isoprene oxidation by NO_3 (R5 and R6b) and IN consumption by OH, O_3 and NO_3. Based on our model calculation, the steady-state NO_3 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~~because of the fast IN+OH reaction rate constants. It is worth noting that RO_2 produced from isoprene + NO_3 (R6) also has competing loss channels for reaction with RO_2 (R7) and with HO_2 (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.

$$C_5H_8 + NO_3 (+ O_2) \rightarrow ONO_2RO_2 \qquad \text{(R6)}$$

$$ONO_2RO_2 + RO_2 \rightarrow ONO_2RO + RO + O_2 \qquad \text{(R7a)}$$

$$ONO_2RO_2 + RO_2 \rightarrow ONO_2ROH + R'CHO + O_2 \qquad \text{(R7b)}$$

$$ONO_2RO_2 + HO_2 \rightarrow ONO_2ROOH \qquad \text{(R8)}$$

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 the 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 the high concentration in the RL as it is formed, and zero deposition removal overnight. The NO_2 concentration is low when the RL is formed at sunset, so contribution from IN production through NO_3 chemistry is small (1-10ppt), a minor fraction compared with the concentration of IN already present in the RL in the evening. Isoprene-NO_3 chemistry can generate IN isomers with a different~~ly~~ 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~~altitude-dependent IN concentration ~~with altitude~~ caused by OH oxidation, as well as possible IN concentration change caused by advection. Therefore, the actual IN concentration may be very different from the calculated results. This is reflected in a comparison of the large RL IN excess relative to surface IN on Jun 26 and 27 (Figure 9), with simultaneous model overprediction of daytime IN on these two days (Figure 8a). Hence, detailed three-dimensional chemical transport models are needed to fully elucidate the production and storage mechanisms of IN in the ambient environment.

4.2 High-NO_x and low-NO_x chemistry during SOAS

OH oxidation was the most important daytime sink for BVOCs during SOAS. As the γ value decreased from 0.95 at 7:00 AM to 0.3 at 1:00 PM (Figure 7b), the BVOC-derived RO_2 radicals are expected to undergo both NO (high NO_x) and HO_2 (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 (Figure 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 PM) were accompanied with a small γ value (~0.3, Figure 7b), significant amount of IN would be oxidized following the HO_2 pathway. A possible reaction scheme is illustrated in Figure 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 NO_2. Although IEPOX can be produced from IN oxidation, the ISOPOOH pathway was still the dominant IEOPOX precursor during this study, due to the higher concentrations of ISOPOOH and its higher yield for IEPOX (~70-80%) (St. Clair et al., 2015). For RO_2 radicals produced from OH addition to IN, 30% will react with NO and 70% will react with HO_2 for a γ value of 0.3 at 1:00 PM.

For the RO_2+NO reaction, Lee et al. (2014b) 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 RO_2+NO reaction will dissociate to make either MACR nitrate or lose NO_2 to form hydroxyacetone and glycoaldehyde. Both Jacobs et al. (2014) and Lee et al. (2014b) 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 RO_2+HO_2 products from IN oxidation are less understood. Alkyl peroxy radical reaction with HO_2 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 $CH_3CH_2O_2$, can form hydroperoxide with almost unity yield (Hasson et al., 2004). However, for peroxy radicals with β carbonyl groups, such as $RC(O)CH_2O_2$, the branching ratio for the OH formation pathway is more than 60% (Hasson et al., 2012; Hasson et al., 2004). 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 RO_2 from IN oxidation has a β-OH group and a β-NO_3 group, both capable of forming internal hydrogen bonding with the hydrogen of HO_2. Therefore, formation of OH and RO radicals may be a significant reaction channel when the RO_2 radicals derived from IN react with HO_2. The closed-shell product from the RO_2+HO_2 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 $C_5H_{11}O_7N$ 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 NO_2 recycling efficiency for IN oxidation, as the detailed RO_2+HO_2 reaction mechanism is unclear. If RO_2+HO_2 reaction forms only hydroperoxide, the NO_2 yield from IN oxidation will be 17%. If RO_2+HO_2 reaction only undergoes the radical formation channel, the NO_2 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 O_3 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 RO_2 to form high NO_x photooxidation products such as IN, MVK and MACR. As the NO_x concentration decreased during the day, the RO_2+HO_2 reactions became more important, and by ~1:00 PM only 30% of the RO_2 react with NO, and thus only 2.7% of the RO_2 would form organic nitrates. The high NO_x concentration in the early morning caused an early IN maximum at 10:00 AM, 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 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. Aerosol uptake could also be an IN sink, but the contribution is expected to be small (Surratt et al., 2010b). Observations during SOAS suggest that the isoprene-derived SOA components were associated with IEPOX and more oxidized organic nitrates, not the first-generation hydroxynitrates (Xu et al., 2015b; Lee et al., 2015).

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While IN were produced and destroyed in the morning through high NO_x chemistry, a major portion of the afternoon IN oxidation process involved low NO_x 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 NO_3^- and trihydroxy hydroperoxide. This process removes NO_x from the atmosphere and helps to shift the photochemical processes further toward the low NO_x regime, forming a positive feedback mechanism to reduce the atmospheric NO_x concentration. However, more experimental studies are required to elucidate the detailed mechanism for the RO_2+HO_2 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., 2015a; Surratt et al., 2010a; Nguyen et al., 2014a), indicating potentially higher SOA burdens from isoprene chemistry in the future. The 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 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 1. Hydroxynitrates from OH-initiated isoprene oxidation (high NO_x).

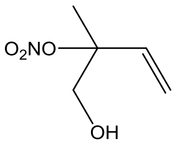
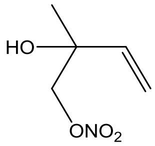
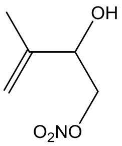
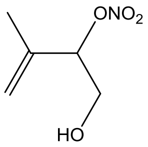
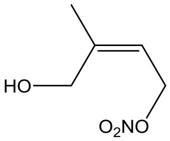
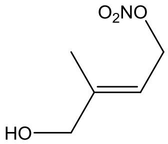
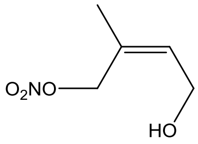
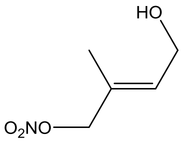
β-INs				
	1,2-IN	2,1-IN	3,4-IN	4,3-IN
δ-INs				
	cis-1,4-IN	*trans*-1,4-IN	*cis*-4,1-IN	*trans*-4,1-IN

Table 2. Initial conditions for IN yield experiments.

Expt. number	Isoprene (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

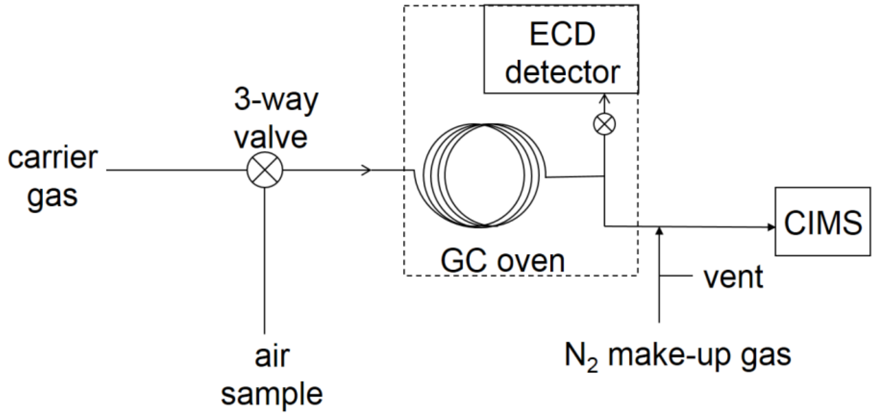


Figure 1. GC-ECD/CIMS setup for the CIMS sensitivity of 1,2-IN relative to 4,3-IN.

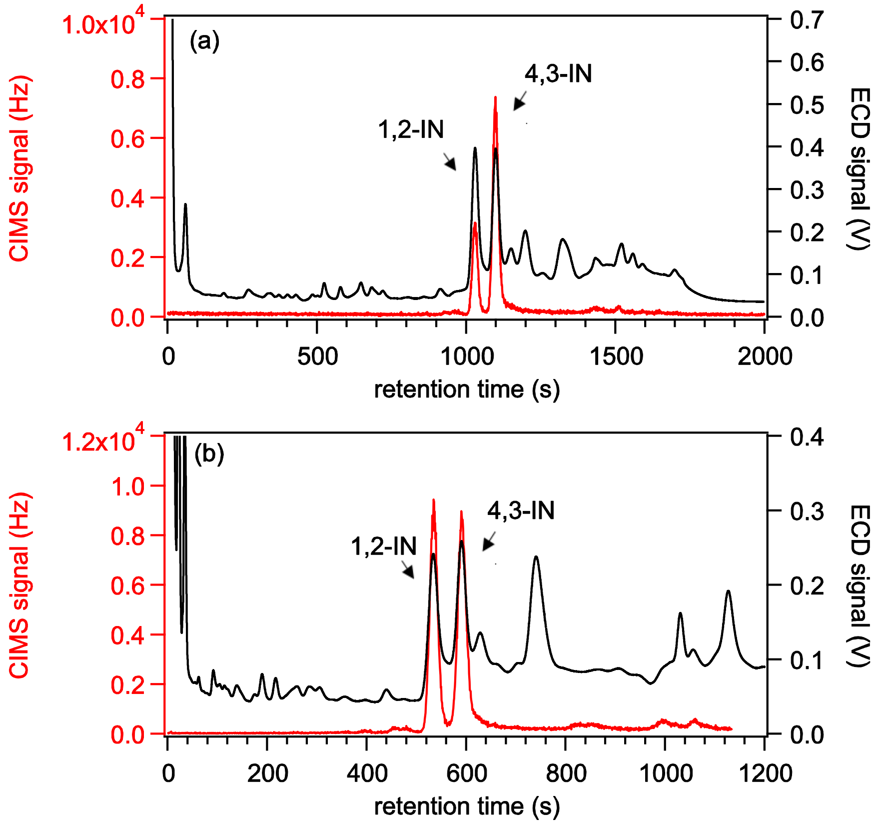


Figure 2. GC-ECD/CIMS chromatogram with water (a) and without water (b) added to the CIMS. The ECD signal is in black and the CIMS signal is in red.

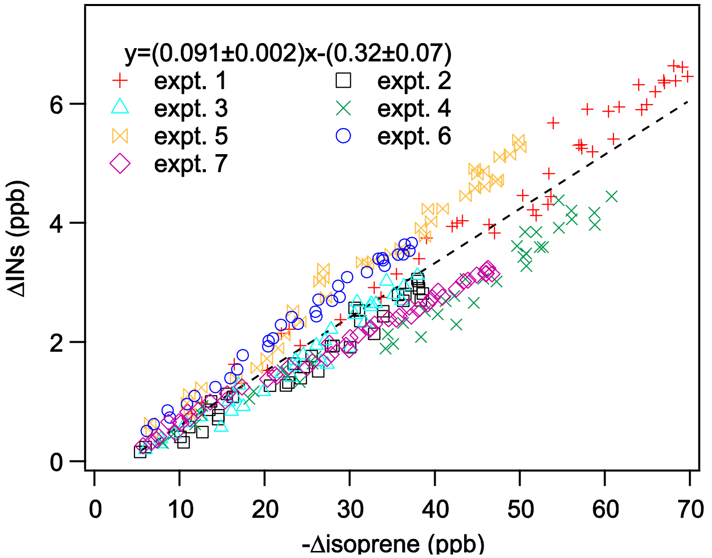


Figure 3. IN and isoprene data for chamber experiments. An average yield of 9% was obtained from data of the seven experiments.

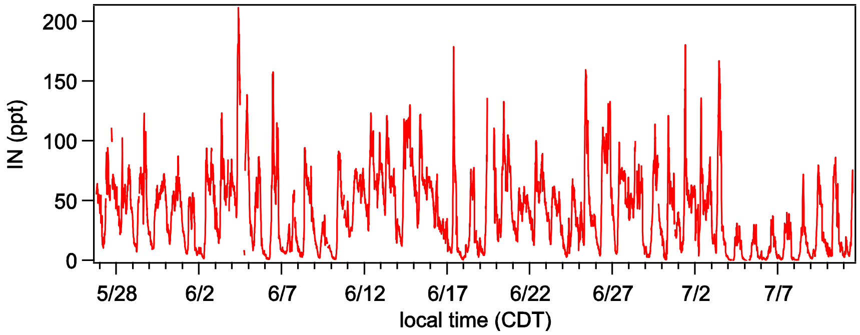


Figure 4. IN observed during SOAS.

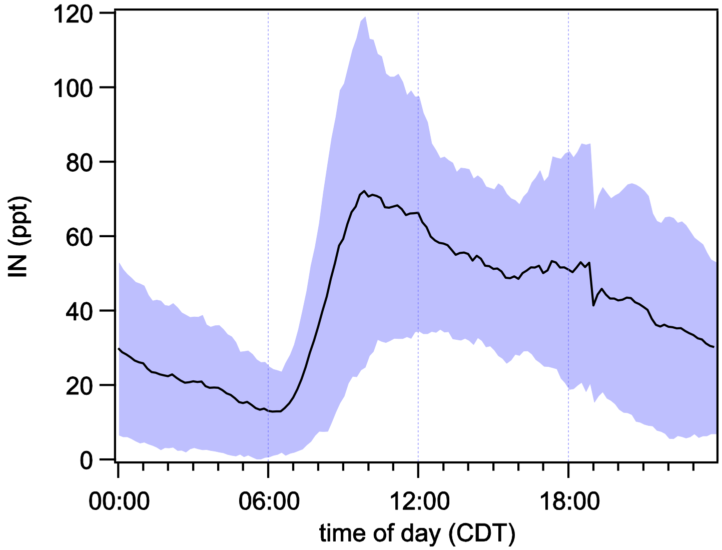


Figure 5. IN diurnal average from May 28 to Jul 11. The blue shade indicates day-to-day variation (1σ). The abrupt drop of concentration at 7 PM is caused by instrument fluctuation during its daily maintenance.

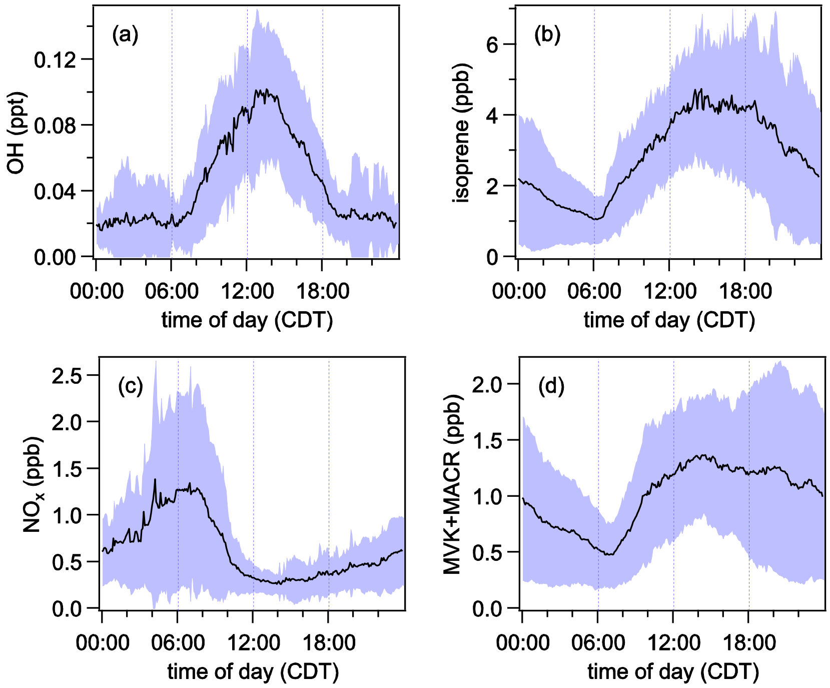


Figure 6. Diurnal average of OH (a, Jun 13 - Jul 3), isoprene (b, Jun 16 - Jul 11), NO_x (c, Jun 1 - Jul 15) and sum of MVK and MACR (d, Jun 16 - Jul 11).

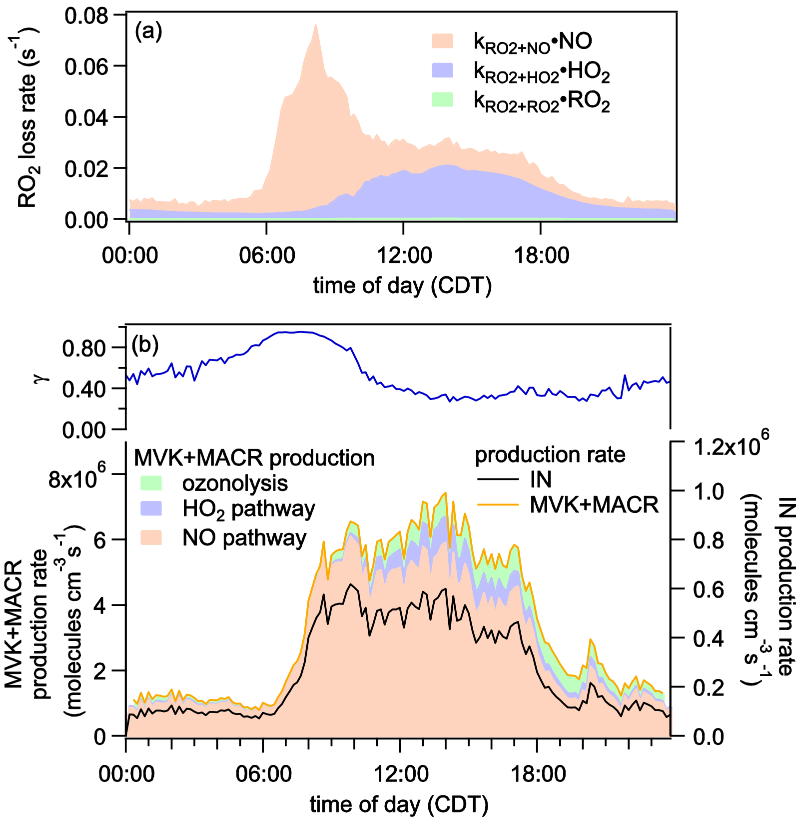


Figure 7. (a) Diurnal average of RO_2 loss rates for reaction with NO, HO_2 and RO_2 from Jun 22 to Jul 7. (b) Diurnal average of γ value and production rates of IN and MVK+MACR from Jun 22 to Jul 7. For MVK+MACR, production from the three reaction channels are shown in different colors.

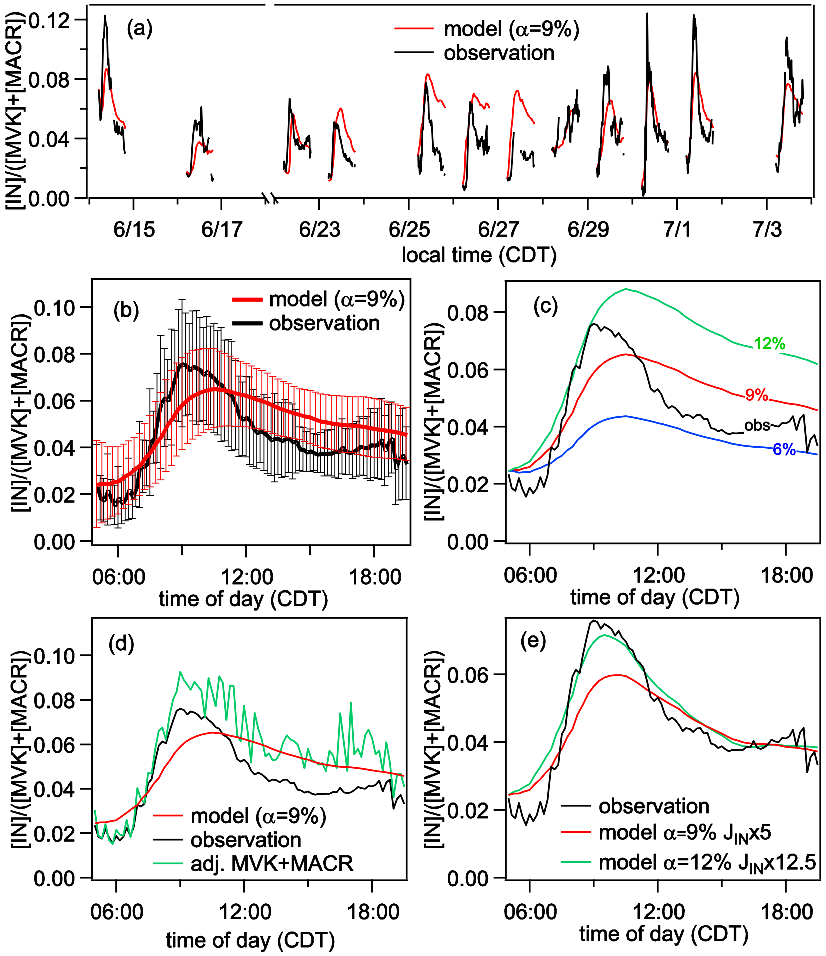


Figure 8. Simulated and observed [IN]/([MVK]+[MACR]) ratio. (a) Results for each selected days. (b) Averaged results over the 12 days. The error bars represent day-to-day variation. (c) Sensitivity test with IN yield set as 6%, 9% and 12% in the model. (d) MVK+MACR data was adjusted by subtracting observed IEPOX+ISOPOOH concentration from observed MVK+MACR concentration. (e) Results with enhanced IN photolysis rate.

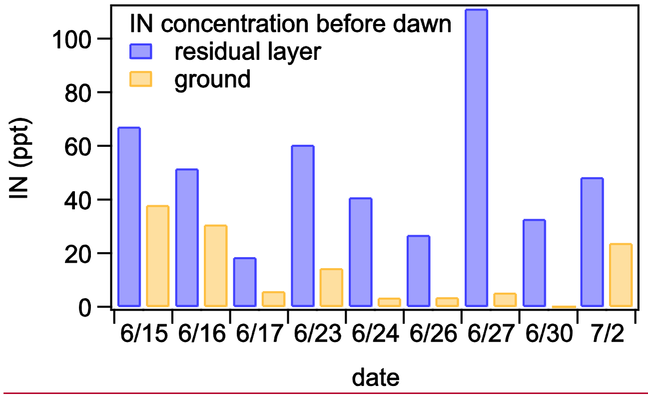


Figure 9 Modeled IN in the residual layer and IN observed near ground before dawn the next day. The model includes IN production from isoprene oxidation by NO_3 and IN consumption by reaction with OH, O_3 and NO_3. The modeled IN may be biased, as concentration change caused by transport is not considered.

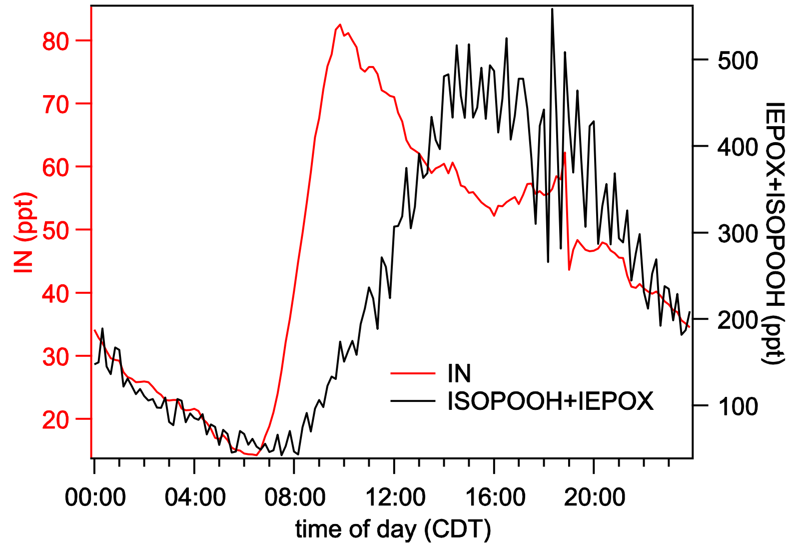


Figure 10 Diurnal averages of IN and ISOPOOH+IEPOX from May 30 to July 4.

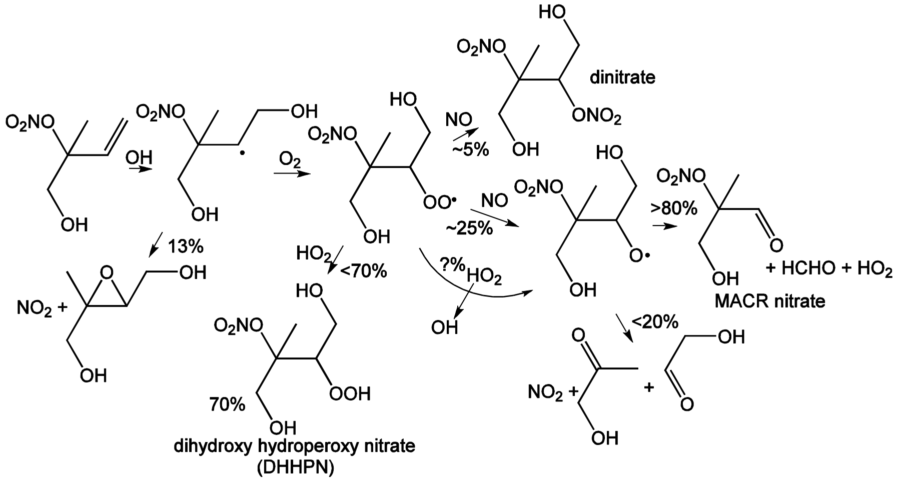


Figure 11 Possible oxidation mechanism for 1,2-IN with γ=0.3.