Key role of NO3 radicals in the production of isoprene nitrates and nitrooxyorganosulfates in Beijing

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Key Role of NO₃ Radicals in the Production of Isoprene Nitrates and Nitrooxyorganosulfates in Beijing


ABSTRACT: The formation of isoprene nitrates (Isn) can lead to significant secondary organic aerosol (SOA) production and they can act as reservoirs of atmospheric nitrogen oxides. In this work, we estimate the rate of production of Isn from the reactions of isoprene with OH and NO₃ radicals during the summertime in Beijing. While OH dominates the loss of isoprene during the day, NO₃ plays an increasingly important role in the production of Isn from the early afternoon onwards. Unusually low NO concentrations during the afternoon resulted in NO₃ mixing ratios during the afternoon. Unusually low NO concentrations during the afternoon resulted in NO₃ mixing ratios of ca. 2 pptv at approximately 15:00, which we estimate to account for around a third of the total Isn production in the gas phase. Heterogeneous uptake of Isn produces nitrooxyorganosulfates (NOS). Two mononitrated NOS were correlated with particulate sulfate concentrations and appear to be formed from sequential NO₃ and OH oxidation. Di- and tri-nitrated isoprene-related NOS, formed from multiple NO₃ oxidation steps, peaked during the night. This work highlights that NO₃ chemistry can play a key role in driving biogenic–anthropogenic interactive chemistry in Beijing with respect to the formation of Isn during both the day and night.

INTRODUCTION

Poor air quality is the biggest environmental factor contributing to premature mortality globally.(1) As earth’s population has grown, the number of people living in urban areas has increased rapidly from 751 million in 1950 to 4.2 billion in 2018.(2) By 2030, the UN estimates that there will be 43 megacities (>10 million inhabitants), with most of them located in developing countries in Africa, Asia, and Latin America.(2) Since many of these locations are situated in the tropics, high average temperatures can lead to significant emissions of biogenic volatile organic compounds (BVOC) to the urban atmosphere, in particular isoprene.(3) Beijing, China, is a well-studied megacity, with significant air quality issues related to particle pollution and ozone (O₃) production. Beijing experiences high average summertime temperatures (ca. 30 °C) and has a high percentage of urban green space (~41% urban green space), which can lead to significant amounts of isoprene being emitted.(5) Photochemical oxidation of isoprene in the presence of high levels of anthropogenic pollutants, in particular nitrogen oxides (NOx) and sulfur dioxide (SO2), can lead to enhanced secondary organic aerosol (SOA) production.(6–21)

A key uncertainty in understanding SOA production from isoprene is the role of isoprene nitrates (Isn). Isn are formed in chain-terminating reactions during oxidation by hydroxyl radicals (OH) in the presence of NO or by nitrate radicals (NO₃). Isn formation can reduce local O₃ production and acts as a sink for atmospheric nitrogen.(22) During the daytime, the reaction of isoprene with OH leads to the formation of hydroxy peroxy radicals (ISOPOO), which can react with NO to form isoprene hydroxy nitrates (IHN), with further reactions leading to a suite of multifunctional Isn species (see Wennberg et al. and references therein).(23) At night, OH radical concentrations are much lower,

![Figure 1.](https://dx.doi.org/10.1021/acs.est.0c05684)

Figure 1. (a) Time series of NO₂ mixing ratio (pptv) measured by the BBCEAS. (b) Time series of isoprene (ppbv) measured by DC-GC-FID. (c) NO₃ loss fraction calculated using measured NO₃ sinks, including photolysis and heterogeneous losses. N₂O₅ aerosol uptake coefficient of 0.022 has been used based on Tham et al. (d) Mean diurnal variation of data shown in (c). (e) Mean diurnal variation of NO₃ mixing ratio (pptv), total production (P_{NO3}), and loss rates (L_{NO3}) (ppbv h⁻¹ and s⁻¹, respectively). VOCs in each classification are given in Table S1.
Recent observations in a boreal forest by Liebmann et al.\textsuperscript{11} under low-NO conditions indicated that daytime alkyl nitrate production from NO\textsubscript{3} chemistry can dominate over OH under certain conditions. Although Beijing (and other megacities) may not be an obvious low-

The NO environment, recent observations indicate that in summer, NO\textsubscript{3} levels were not measured using a proton transfer mass ion in the 1

A time-of-flight chemical ionization mass spectrometer (ToF-CIMS) was used to measure gas-phase isoprene nitrates in real time.\textsuperscript{40} Isoprene carbonyl nitrates (INC) was measured using gas-chromatography negative-ionization mass spectrometry (GC-NIMS).\textsuperscript{31,42} Nitric oxide (NO) was measured via chemiluminescence with a Thermo Scientific

Figure 2. Average diurnal of (A) isoprene loss rate to NO\textsubscript{3} (black) and OH (red) in ppbv h\textsuperscript{-1}. (B) Calculated ISN production rate from O\textsubscript{3} (blue), NO\textsubscript{3} (black), OH (red), and total (green). (C) OH concentration (red, molecules cm\textsuperscript{-3}), measured by FAGE) and isoprene mixing ratio (green, ppb, measured by DC-GC-FID). (D) C\textsubscript{5}H\textsubscript{9}NO\textsubscript{2} (blue) and C\textsubscript{5}H\textsubscript{10}NO\textsubscript{2} (black) measured by I-CIMS and the sum of cis (Z) and trans (E) δ-[1,4] and δ-[4,1]-isoprene carbonyl nitrates (INC, red) was measured by GC-NI-MS. See the SI for a discussion of the calibration of I-CIMS ions.

NO levels in the afternoon can often drop to below 1 ppbv, and on some days <0.1 ppbv, as a result of reactions with ozone and other unknown chemical reactions.\textsuperscript{32} Thus, daytime nitrate production from NO\textsubscript{3} could be important in other megacities that also experience low NO conditions during the day and high VOC levels. There are few measurements of speciated ISN in urban areas, where isoprene can be emitted from urban plants and green spaces.\textsuperscript{22,33,34} In this paper, we show that NO\textsubscript{3} radical chemistry is important for the production of ISN in Beijing during summer, both during the day and at night, using a comprehensive suite of gas- and particle-phase chemical observations taken as part of the U.K.-China Atmospheric Pollution and Human Health in a Chinese Megacity (APHH-China) program during the summer of 2017.

**MATERIALS AND METHODS**

Time-resolved aerosol filter samples were collected between May 18 and June 24, 2017 at the Tower Section of the Institute of Atmospheric Physics (IAP) in Beijing, China.\textsuperscript{35} The site is typical of central Beijing, with several roads nearby, a canal to the south, and several areas of green space to the south and east. Three aerosol filter samples were collected for 3-h integrated periods between 08:30 and 17:30, and one additional sample taken overnight (17:30–08:30); see Table S2 for sampling times. Samples were collected at a height of 8 m on top of a building at the IAP complex. The samples were collected on preconditioned (500 °C for 5 h) quartz filters (8 × 10 in.) using an ECOTECH HiVOL 3000 with a selective PM\textsubscript{2.5} inlet. Filter samples were extracted in the laboratory into high-purity water and analyzed using an Ultimate 3000 ultra pressure liquid chromatography coupled to a Q-Exactive Orbitrap MS, with heated electrospray ionization (UPLC-ESI-MS\textsuperscript{5}) using the method described in Bryant et al.\textsuperscript{36} Further details on the method used for extraction, analysis, and calibration can be found in the Supporting Information (SI). It should be noted that using surrogate standards for calibration can lead to uncertainties, but authentic organosulfate (OS) standards with similar retention times have been used in this study to minimize this effect.\textsuperscript{37-39} Based on the previous investigation of the ionization efficiency of organosulfates and matrix effects from aerosol samples, we estimate a total uncertainty of 60% on NOS concentrations.\textsuperscript{36} A time-of-flight chemical ionization mass spectrometer (ToF-CIMS) was used to measure gas-phase isoprene nitrates in real time.\textsuperscript{40} Isoprene carbonyl nitrates (INC) was measured using gas-chromatography negative-ionization mass spectrometry (GC-NIMS).\textsuperscript{31,42} Nitric oxide (NO) was measured via chemiluminescence with a Thermo Scientific

**RESULTS AND DISCUSSION**

**Nitrate Radical Production and Loss.** The comprehensive measurement suite available allows the investigation of the dominant production and loss mechanisms for NO\textsubscript{3} in Beijing. Figure 1a shows the mixing ratio of NO\textsubscript{3} radicals measured by the BBCEAS. The average NO\textsubscript{3} mixing ratio was 5 pptv, with a standard deviation of 10 pptv. A strong diurnal profile was observed, shown in Figure 1e, with a peak at 21:00–23:00 and a minimum around 06:00–08:00. The NO\textsubscript{3} production and loss rates were calculated using the measured O\textsubscript{3} and NO\textsubscript{3} concentrations and measurements of known NO\textsubscript{3} sinks,
including reaction with VOCs, photolysis, and loss via N₂O₅ heterogeneous uptake. More details on these calculations are provided in the SI. High ozone mixing ratios (up to 180 ppbv) in Beijing resulted in high NO₃ production rates of the order of 4 ppbv h⁻¹, peaking in the late afternoon and early evening (Figure 1e). High daytime NO₂ loss rates, owing to rapid photolysis and reaction with NO, led to an average mixing ratio of ~2 pptv of NO₃ into the afternoon (Figure 1e). It is often assumed that daytime reactions of NO₃ with hydrocarbons are negligible due to the dominance of loss processes over production. High levels of isoprene were observed in Beijing, shown in Figure 1b, with an average midday mixing ratio around 1 ppbv and a maximum of 2.7 ppbv, and so its reaction can compete as a NO₂ loss mechanism during the day. Figure 1c shows the fractional loss of NO₃ calculated from measurements of various NO₃ sinks; the absolute loss rates are also shown in Figure S3. Reaction with NO and photolysis dominate the loss rate of NO₃ in Beijing. The mean NO₃ loss to isoprene is around 5% across the entire measurement period (Figure 1d), but higher fractional loss rates were observed on some afternoons (Figure S4) with a maximum of 22% prior to sunset on June 14 (Figure S5).

Isoprene Nitrate Production. The main daytime sink of isoprene (ISOP) is its reaction with OH radicals, with the calculated loss rate of isoprene (LISOP+OH = kOH[OH][ISOP]) peaking at about 3.7 ppbv h⁻¹ at midday, as shown in Figure 2A. As a result of high daytime emissions of isoprene, its loss rate via reaction with NO₃ (LISOP+NO₃ = kNO₃[NO₃][ISOP]) was highest between 13:00 and 18:00, as shown in Figure 2A, with a maximum loss rate of isoprene of 160 pptv h⁻¹ in the afternoon. The loss of isoprene from reaction with O₃ was calculated to be a minor pathway, representing less than 10% of LISOP throughout the day.

The production rate of nitrates from isoprene can be estimated using eqs 1 and 2

\[ P_{ISPN+OH} = a_1 k \left[ OH \right] \text{ISOP} \]  
\[ P_{ISPN+NO} = a_2 k \left[ NO \right] \text{ISOP} \]

where \(a_1\) and \(a_2\) are the oxidant-specific relative yields of IsN, \(k_1\) and \(k_2\) are the rate constants for the reaction of isoprene with OH (1.0 \( \times \) 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 298 K) and NO₃ (5.6 \( \times \) 10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 298 K), respectively.\(^{50}\) During the afternoon in Beijing, Newland et al.\(^{12}\) showed that the fraction of the peroxo (RO₂) radicals formed from isoprene + OH, reacting with NO can be as low as 65% (f NO = 0.65), with the remainder reacting with HO₂, RO₂, or undergoing isomerization. Therefore, the production rate of IsN from OH chemistry calculated in eq 1 should be multiplied by f NO during the afternoon as shown in eq 3. The hourly f NO values used for Beijing were taken from Newland et al.\(^{12}\)

\[ P_{ISPN+OH} = a_1 k \left[ OH \right] \text{ISOP} \times f \text{NO} \]  

There is a degree of uncertainty in the values of the total first generation ISN yields, \(a_1\) and \(a_2\), in the literature, and a discussion of the recent literature is given in the SI, Section S4. We use \(a_1 = 0.11\) for isoprene + OH/NO₃, the most recent IUPAC recommended value,\(^{35}\) and \(a_2 = 0.76\) from isoprene + NO₃ from Schwantes et al.\(^{25}\) (see the SI for discussion of values used here). A sensitivity analysis was also carried out using a range of \(a_1\) and \(a_2\) values, shown in the SI, but the overall trends in the ISN production are similar under all conditions. The yield of ISN from the reaction of isoprene with O₃ is uncertain. The \(P_{ISPN+O} \) was calculated following Liebmann et al.,\(^{31}\) where the ozonolysis was assumed to lead to a 100% yield of RO₂ radicals and the OH ISN yield (\(a_1 = 0.11\)) was used. The total calculated ISN production rate (\(P_{ISPN+O} = P_{ISPN+OH} + P_{ISPN+NO} + P_{ISPN+O} \)) is shown in Figure 2B, with a maximum of 353 pptv h⁻¹ at 14:00. The relative contributions of the three pathways to \(P_{ISPN} \) are shown in Figure S6. O₃ represents a minor pathway of ISN production in Beijing during the measurements, with an average \(P_{ISPN+O₃} \) of 2.2% and a maximum of 5.8% at 18:00. Therefore, the following discussion focuses solely on the comparison of IsN production from reaction with OH and NO₃ radicals.

The calculated ISN production rates are shown in Figure 2B, with \(P_{ISPN+OH} \) shown in red and \(P_{ISPN+NO₃} \) shown in black. At midday, \(P_{ISPN total} \) is 480 pptv h⁻¹, with approximately 82% from the OH + NO₃ chemistry (\(P_{ISPN+OH} \)) and 16% from NO₃ oxidation (\(P_{ISPN+NO₃} \)), as shown in Figure S6. The I-CIMS measured the sum of IHN ([C₂H₃NO₃]), the first-generation nitrates formed from isoprene + OH oxidation. The average diurnal observed is shown in black in Figure 2D, and peaked at midday at around 120 pptv, before dropping off in the late afternoon to a minimum overnight as isoprene was depleted.\(^{36}\)

By 16:00, \(P_{ISPN total} \) dropped to ca. 210 pptv h⁻¹ as a result of the low-NO₃ conditions in the afternoon and a reduction in the isoprene mixing ratios. At 16:00, 40% of the calculated \(P_{ISPN total} \) was from NO₃ + isoprene chemistry. Observations of f-[1,4] and f-[4,1]-isoprene carbonyl nitrates (INC) formed from NO₃ chemistry indicate that these species peak in the early evening (red line in Figure 2D). However, even though they are likely to undergo fast photolysis and rapid reaction with OH,\(^{37}\) they are present during the daytime in low concentrations indicating daytime production of ISN from isoprene + NO₃ chemistry. A similar trend is seen in C₂H₃NO₃ (black line in Figure 2D), which is likely to be a mixture of ISN produced from NO₃ chemistry (isoprene nitroxy hydroperoxide (INP), isoprene nitrooxy hydroxypoxide (INH), and isoprene dihydroxyantrate (IDHN)).\(^{25}\)

The mixing ratios of the ISN species will be controlled by a number of processes (secondary chemistry, photolysis, availability of co-reactants) and thus there is unlikely to be a direct correlation between them and the ISN production rate. The total mixing ratio of ISN observed was lower than the theoretical ISN production rate, likely as a result of loss processes and measurement of a small subset of potential ISN species.

Table 1. Molecular Formulae, Negative-Ion Masses ([M – H]⁻), Retention Times (RT), Time-Weighted Means (ng m⁻³), Maximum and Minimum Concentration of NOS Observed in Beijing

<table>
<thead>
<tr>
<th>isoprene tracer</th>
<th>[M – H]⁻</th>
<th>RT (min)</th>
<th>time-weighted mean (ng m⁻³)</th>
<th>Max (ng m⁻³)</th>
<th>Min (ng m⁻³)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₄O₂NS</td>
<td>260.0082</td>
<td>0.86</td>
<td>12.6</td>
<td>154.1</td>
<td>0.10</td>
<td>19</td>
</tr>
<tr>
<td>C₃H₄O₂NS</td>
<td>273.9874</td>
<td>0.94</td>
<td>9.17</td>
<td>53.8</td>
<td>BD</td>
<td>47</td>
</tr>
<tr>
<td>CH10011N12S</td>
<td>304.9933</td>
<td>2.18</td>
<td>1.04</td>
<td>8.62</td>
<td>BD</td>
<td>19</td>
</tr>
<tr>
<td>CH10011N12S</td>
<td>304.9933</td>
<td>1.89</td>
<td>0.83</td>
<td>7.69</td>
<td>BD</td>
<td>19</td>
</tr>
<tr>
<td>CH10011N12S</td>
<td>304.9933</td>
<td>1.56</td>
<td>0.42</td>
<td>2.90</td>
<td>BD</td>
<td>19</td>
</tr>
<tr>
<td>CH10011N12S</td>
<td>304.9933</td>
<td>3.60</td>
<td>0.31</td>
<td>3.32</td>
<td>BD</td>
<td>19</td>
</tr>
<tr>
<td>CH4O₂NS</td>
<td>349.9783</td>
<td>5.90</td>
<td>0.19</td>
<td>2.04</td>
<td>BD</td>
<td>25</td>
</tr>
<tr>
<td>CH4O₂NS</td>
<td>349.9783</td>
<td>4.95</td>
<td>0.09</td>
<td>0.17</td>
<td>BD</td>
<td>25</td>
</tr>
<tr>
<td>CH4O₂NS</td>
<td>349.9783</td>
<td>5.34</td>
<td>0.008</td>
<td>0.10</td>
<td>BD</td>
<td>25</td>
</tr>
</tbody>
</table>

a BD, below detection. The references indicate previous publications where these molecular formulae were observed in isoprene oxidation chamber experiments.

Even though only a small fraction of isoprene reacts with NO₃ during the afternoon (a few percent, as shown in Figure 2A), it can represent a significant source of ISN, contributing an average of 32% to the measured NO₃ over the afternoon (12:00–19:00). In the early evening and into the night, the contribution of \(P_{ISPN+NO₃} \) to the total \(P_{ISPN total} \) increases rapidly (average 86% between 19:00 and 05:00) as the photochemical production of OH drops significantly and NO₃ concentrations increase. Once produced, the gas-phase ISN can react further or partition into the particle phase either directly, depending on their volatility, or undergo heterogeneous uptake via the reaction with acidic particles, including the formation of nitroxyorganosulfates (NOS). To study the presence of isoprene SOA in PM₂.₅, we collected particles onto filters and analyzed the water-soluble extracts using UPLC-ESI-MS. This method is not particularly suited to ISN, owing to low signal intensity using ESI and the possibility of hydrolysis of ISN in aqueous solutions.
However, the sulfated analogues (NOS) give a strong signal and allow us to investigate the factors that can affect the production of SOA from isoprene nitrates in Beijing.

Particulate isoprene Nitrooxyorganosulfates (NOS). Nine isoprene-derived NOS compounds were observed in the Beijing samples and their mean, median, and maximum observed concentrations are shown in Table 1. Two isoprene-derived mono-nitrated tracers (C₅H₇NO₃S, molecular weight (MW) 261 and C₆H₆NO₃S, MW 275) followed similar temporal trends as other OS and with a strong correlation with particulate sulfate as discussed below.²⁶ Four isoprene-derived di-nitrated NOS isomers (C₆H₉NO₃S, MW 306) and three tri-nitrated NOS isomers (C₇H₁₀NO₃S, MW 351) were also observed, all showing a strong enhancement during the night.

Mono-nitrage NOS. A NOS (C₅H₇NO₃S, MW 261) consistent with 2-methyltetrol nitrooxyorganosulfate was observed, and the time series is shown in Figure 3a. This species had a mean concentration of 12.6 ng m⁻³, a standard deviation of 19.6 ng m⁻³ and a maximum of 154 ng m⁻³. This mean concentration is similar to that of 2-hydroxy-5-methyltetrol nitrate (C₅H₉NO₃S, MW 261), a standard deviation of 19.6 ng m⁻³, a mean concentration of 12.6 ng m⁻³, and a maximum of 154 ng m⁻³. This mean concentration is similar to that of 2-methylglyceric acid (C₅H₈NO₃S, MW 275).

Table 1. Proposed Formation Pathways of Mono-Nitroated OS and Di-Nitroated OS Species Observed in the Aerosol from the NOS Initiated Oxidation of Isoprene²⁵

Scheme 1. Proposed Formation Pathways of Mono-Nitroated OS and Di-Nitroated OS Species Observed in the Aerosol from the NOS Initiated Oxidation of Isoprene²⁵

![Scheme 1](image)

Note that only one of six possible INP isomers is shown, for simplicity, with δ-[1,4]-INP and β-[1,2]-INHE the dominant isomers observed in Schwantes et al.²⁵ afternoon, as shown in box whisker plots in Figure 4A, although there is not a very strong diurnal profile. This NOS species was observed to have a moderate correlation with particulate sulfate (R² = 0.61) shown in Figure S7. This NOS species also correlated moderately to strongly with other OS species formed from isoprene oxidation by OH, observed in Beijing (2-MT-OS, R² = 0.51; 2-methylglyceric acid-OS, R² = 0.58; C₅H₆O₃S, MW 198, R² = 0.80). Wang et al.³⁵ also observed that this NOS species correlated well with other isoprene-derived OS at Changping, a site 38 km northeast of Beijing. We propose that this NOS compound is formed from the acid-catalyzed heterogeneous oxidation of isoprene nitrooxyhydroxypexide (INHE),²⁶ as shown in Scheme 1.

The reaction of isoprene with NO radicals leads to isoprene nitrooxy radicals (INO₃). Under the low concentrations of NO observed in this study, INO₃ can react with HO₂, leading to the formation of isoprene nitrooxy hydperoxide (INP), as shown in the central section of Scheme 1. Using the observed concentrations of NO and HO₂ measured, we estimated that up to 10–15% of INO₃ can react with HO₂ during low NO afternoons in Beijing, as shown in Figure S8. There are six INP isomers possible and only the most abundant isomer (δ-[1,4]-INP) observed by Schwantes et al.²⁵ is shown. The reaction of INP with OH radicals, followed by OH recycling, can lead to INHE (δ-[4,1]-INHE and δ-[1,2]-INHE) in a similar way to the formation of isoprene-derived epoxypidols (IEPOX) from the reaction of OH with isoprene hydroxypexides (ISOPPOOH).³⁴ Schwantes et al.²⁵ also showed that INHE could undergo reactive uptake to highly acidiﬁed aerosol, similar to IEPOX.

![Figure 4](image)

Figure 4. Box and whisker plots of observed NOS concentrations separated by the time of day the ﬁlter was collected: (A) C₅H₇NO₃S, (B) C₆H₆O₃NS, (C) C₆H₉NO₃S, and (D) C₇H₁₀NO₃S. The filter midpoints were split into diurnal proﬁles. This ICN species can then react with NO₃ or OH, leading to the formation of the observed NOS species via an isoprene nitrooxy hydroxy-α-lactone (INHL) species, as shown in Scheme S1. This route is similar to the formation of 2methylglyceric acid (2-MG) from isoprene + OH derived hydroxymethyl-methyl-α-lactone (HMML).¹⁶ The second proposed route is the formation of this species as a result of heterogeneous oxidation of 2-methyltetrol nitrate (C₅H₇(NO₃)S), as shown in Scheme S2. This route has recently been shown to be an important pathway to form the nonnitrated OS analogues, with 2-MT-OS undergoing saltgout to the surface of particles making it susceptible to heterogeneous OH oxidation.³⁵ The carbonyl species formed may then undergo cyclization to form a NOS hemiacetal species. Further work is needed to determine which of these pathways are important.
for the formation of this abundant isoprene derived NOS species in polluted environments.

Di- and Tri-Nitrated NOS. Four of the isoprene-derived NOS species are di-nitrate isomers (C₅H₁₀NO₃S; MW 306, with retention times 1.56, 1.86, 2.18, and 3.6 min) and three are tri-nitrate isomers (C₅H₁₀NO₄S; MW 351, with retention times 5.34, 5.49, and 5.90 min). These structural isomers result from the different INO₂ radicals that can form during isoprene + NO₃ oxidation. However, the product-ion mass spectra (MS²) provided only a few ions related to the loss of sulfate and nitrate and could not be used to determine the position of the groups. The time series of the sum of the diand tri-nitrated NOS is shown in Figure 3c,d, respectively. The sum of the four isoprene di-nitrate NOS isomers had an average concentration of 2.6 ng m⁻³, a standard deviation of 2.6 ng m⁻³, and a maximum of 23 ng m⁻³. The tri-nitratated NOS species were observed at much lower concentrations, with an average sum of 0.2 ng m⁻³, a standard deviation of 0.3 ng m⁻³, and a maximum of 2.3 ng m⁻³. These isoprene-derived NOS exhibited moderate to strong correlations with each other, as shown in Figure S7 (R² = 0.76–0.99).

The di-nitrated NOS (MW 306) species show a strong enhancement at night, as shown in Figure 4C, with the mean nighttime concentration (3.43 ng m⁻³), around 7 times higher than during the afternoon (0.47 ng m⁻³). These NO₃ tracers have all previously been observed in chamber studies of NO₃ oxidation of isoprene.¹⁹⁻²⁵,³⁰ The same di-nitrates have also been observed during the oxidation of isoprene by OH in the presence of NOₓ but this is assumed to be a minor NOS formation pathway under the conditions observed in Beijing owing to their significant enhancement in the night-time samples. The tri-nitrated NOS is also elevated at night, as shown in Figure 4D, with very low concentrations observed in the afternoon.

Ng et al.²⁶ proposed the formation of di- and tri-nitrated OS via the formation of an isoprene hydroxynitrate (IHN) from INO₂ + INO₂ self-reactions after the initial NO₃ attack. A second NO₃ oxidation step at the other double bond then leads to the formation of dihydroxy-dinitrates, again via the reaction with INO₂ radicals. A subsequent unknown reaction step with particulate sulfate is then postulated to lead to NOS formation. Here, we propose an alternative mechanism where this species is formed via heterogeneous uptake of a dinitrated epoxide, as shown in the lower section of Scheme 1. Similar to the mono-nitrate formation, the NO₃ reaction with isoprene leads to INO₂, and the reaction with HO₂ leads to the isoprene nitrooxy hydroperoxide (INO). Subsequent addition of a second NO₃ at the C₂ position of the remaining double bond leads to an alkyl radical on the C₃ position. This radical then eliminates OH to form isoprene di-nitrate epoxide (IDNE), as proposed in Kwan et al.²⁷,²⁸ Again, this mechanism is very similar to the production of IEPOX from ISOPOOH,²⁴ except in this case rather than being OH neutral (as in the mono-nitrate route to INH in Scheme 1), it can act as a net source of OH radicals at night. Using an OH yield of 0.15, based on Wennberg et al.,²⁹ calculated the OH production rate from this pathway during sunset and early evening (19:00–22:00) was relatively small, of the order of 2–5 × 10⁶ molecules cm⁻³ s⁻¹. The resulting IDNE species can then undergo heterogeneous uptake to acidic aerosols to form either di-hydroxy-di-nitrites via the reaction with H₂O⁺ or di-nitrooxy hydroxy OS from the reaction with sulfate. The isoprene-derived di- and tri-nitrated NOSs exhibited a strong diurnal profile as shown in Figure 4c,d, peaking in the night-time samples, suggesting their formation is a result of multiple steps of NO₃ oxidation. This is in contrast to the INH-derived mono-nitrate outlined above that formed as a result of NO₃ oxidation followed by OH oxidation. The correlation of the di- and tri-nitrated NOS with particle sulfate is much weaker than the mono-nitrate NOS, as shown in Figure S7 (R² = 0.07–0.45). There is no correlation with the average night-time NO₃ mixing ratio (R² = 0.10), but there is a weak correlation with the maximum production rate of NO₃ (Pₐₙ₅), R² = 0.29 calculated during each filter sampling period. Production of these NOS species is predicted to be highest just after sunset (ca. 19:15–19:30), where residual isoprene can react with increased levels of NO₃ as shown in Figure 1e, resulting from lower levels of photolysis. The production will then reduce rapidly as the isoprene and NO₃ are consumed, with the mean NO₃ dropping to sub-pptv values by 05:00 (see Figure 1e). The strong enhancement of the observed di- and tri-nitrated NOS at night, in comparison to the INHE-related mono-nitrate, may indicate that their common precursor INP reacts with OH radicals during the day, and the products that require two NO₃ oxidation steps therefore only form when OH levels drop after sunset. The formation route of the tri-nitrated species remains uncertain.

The diurnal profile of the di- and tri-nitrated NOS species both show a surprisingly rapid drop in the concentration during the daytime. In a previous study of highly oxidized organic nitrates using CIMS, the optimum model-observation agreement was achieved using a strong atmospheric lifetime of the order of 2–4 h.²⁹ Therefore, the diurnal profile seen in Beijing is likely the result of a rapid in-particle loss of di- and tri-nitrated NOS, through processes such as hydrolysis or oxidation.⁵⁹,⁶⁰ This may lead to particle-phase inorganic nitrate formation and act as a minor sink of atmospheric NO₃ in Beijing. The drop in concentration of these species during the day may be partly due to the expansion of the boundary layer in the morning; however, this is not sufficient to explain the trends. On most days, there was also an appreciable amount of these NOS species in the morning samples, as shown in Figure 3c; and on a few days, the concentration of di-nitrated OS (MW 306) increased in the morning sample. The average diurnal profile of the observed mixing layer height during the campaign shows a shallow nocturnal boundary layer with a minimum of around 250 m at midnight, then increasing from around 08:00 to a maximum of around 1000 m at 15:00 (Figure S9). A recent study has shown the efficient formation of IsN in a polluted residual layer over Sacramento, California.⁶¹ We suggest that the relatively high abundance of these species during the early morning sample may be a result of mixing down of regionally produced NOS from the nocturnal residual layer during the collapse of the nocturnal boundary layer (Figure S9).

Our observations show that the reaction of isoprene with NO₃ leads to the formation of isoprene-derived nitrates in both the gas and particle phases in Beijing and that the nitrate radical plays a key role in the formation of IsN both during the day and at night. The mono-nitrated isoprene NOS identified are predominately formed in the late afternoon from the reaction with NO₃ and then OH radicals, with their concentration also influenced strongly by particulate sulfate availability. In contrast, the abundance of the di- and trinitrated isoprene NOS species, in summertime, is driven by both local night-time NO₃ chemistry, most likely in the early evening when the nitrate radical concentrations are increasing (and OH decreasing) as the sun goes down and isoprene is still present in reasonable amounts, and the mixing down of aged aerosol in the morning from more regional sources as the nocturnal boundary layer collapses. Unfortunately, the long nocturnal filter sampling time (15 h) in this study does not allow the full dynamics of the night-time formation of NOS to be observed and increased temporal resolution is needed to determine the relative role of isoprene, NO₃, and sulfate aerosol to and NOS formation in Beijing and other megacities. The measurements were taken at 8 m and so represent surface processes close to the emission of both isoprene and NO. Further work is needed to understand the extent of this chemistry throughout the boundary layer and the role of nonlocal sources on the isoprene IsN and NOS.

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Field instrumentation (Section S1); offline analysis (Section S2); calculations of NO₃ production and loss (Section S3); isoprene nitrate yields used in PlsN calculations (Section S4); INO₂ reaction with HO₂ and NO (Section S5); median diurnal variation of NO₃ loss fraction calculated using measured NO₃ sinks, including photolysis and
heterogeneous losses (Figure S1); calculated percentage of IN production (Figure S2); NO\textsubscript{2} loss rate calculated using measured NO\textsubscript{2} sinks (Figure S3); probability density function of the loss fraction of NO\textsubscript{2} (Figure S4); fractional NO\textsubscript{2} loss rate on the 14/06/2017, calculated using measured NO\textsubscript{2} sinks (Figure S5); fractional contribution to the calculated isO\textsubscript{3} production rate (Figure S6); coplot containing the nitrooxy organosulfates measured by UPLC-MS\textsuperscript{2}−; particulate sulfate measured via an aerosol mass spectrometer (AMS) and the product of ozone and sulfate (Figure S7); plot of k\textsubscript{OH} (k\textsubscript{OH}/k\textsubscript{SO}) (Figure S8); average diurnal profile of boundary layer height (Figure S9); reactivity included in NO\textsubscript{3} loss calculation (Table S1); start, end and midpoint date times for the filters collected and analysed for this study (Table S2) (PDF)

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Heterogeneous Hydroxyl Radical Oxidation of Isoprene

Heterogeneous N2O5 Uptake Coefficient and Production of N2O5 and ClNO2 in Summer in Beijing, China.


