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

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Key Role of NO$_3$ Radicals in the Production of Isoprene Nitrates and Nitroxyorganosulfates 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 NO$_3$ radicals during the summertime in Beijing. While OH dominates the loss of isoprene during the day, NO$_3$ plays an increasingly important role in the production of IsN from the early afternoon onwards. Unusually low NO concentrations during the afternoon resulted in NO$_3$ 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 nitroxyorganosulfates (NOS). Two mono-nitrated NOS were correlated with particulate sulfate concentrations and appear to be formed from sequential NO$_3$ and OH oxidation. Di- and tri-nitrated isoprene-related NOS were formed from multiple NO$_3$ oxidation steps, peaked during the night. This work highlights that NO$_3$ 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 (O$_3$) production. Beijing experiences high average summertime temperatures (ca. 30 °C) and has a high percentage of urban green space (>41% urban green space),(4) 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 and in areas with sufficient NO$_x$ to form NO$_2$ rapidly,(6) oxidation by NO$_3$ radicals often becomes a more important route for loss of isoprene. Reaction with NO$_3$ leads to the production of isoprene nitroxy perox radicals (INO$_x$), which can then go on to form a range of IsN species via reactions with HO$_2$, RO$_2$, and NO.(5,25) During the daytime, volatile organic compound (VOC) + NO$_3$ reactions are usually limited by the fast photolysis of NO$_3$ and its reaction with NO. IsN have recently been observed in rural and forested regions using online chemical ionization mass spectrometry. Ayres et al. measured organic nitrates at a rural forested site in Alabama as part of the SOAS campaign, where emissions were dominated by biogenic VOCs.(27) They identified a number of IsN (C$_5$H$_9$NO$_5$, C$_5$H$_9$NO$_4$, C$_4$H$_9$NO$_5$) and they were mainly found in the gas phase. Massoli et al. identified highly oxygenated molecules (HOMs) from isoprene during the same project.(28) Significant amounts of highly oxidized IsN were also identified, with some species having a strong correlation with SO2 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 (NO$_3$). IsN formation can reduce local O$_3$ 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,
Recent observations in a boreal forest by Liebmann et al.\textsuperscript{31} 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-

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{2} (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{3}H\textsubscript{6}NO\textsubscript{2} (blue) and C\textsubscript{3}H\textsubscript{5}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 environment, recent observations indicate that in summer, 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 cities, 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 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.\textsuperscript{2}) 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-ESIMS\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 organosulphates (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{40} A time-of-flight chemical ionization mass spectrometer (ToF-CIMS) using an iodide ionization system was used to measure gas-phase isoprene nitrates in real time.\textsuperscript{41} Isoprene carbonyl nitrates (INC) was measured using gas-chromatography negative-ionization mass spectrometry (GC-NIMS).\textsuperscript{42,43} Nitric oxide (NO) was measured via chemiluminescence with a Thermo Scientific 42i Trace Level NO\textsubscript{X} analyzer with a limit of detection <50 ppt (120 s averaging time). NO\textsubscript{3} was measured via a cavity attenuated phase shift (CAPS) spectrometer (Teledyne T500U CAPS Trace-level NO\textsubscript{3} analyzer; the limit of detection was <40 ppt, averaging time, 60 s). Volatile organic compounds (VOCs) were measured hourly using dual-channel gas chromatography with flame ionization detection (DC-GC-FID)\textsuperscript{44} with a limit of detection in the 1–5 ppt range. The sum of monoterpenes was measured using a proton transfer mass spectrometer (PTR-MS).\textsuperscript{45} Measurements of OH, HO\textsubscript{2}, and RO\textsubscript{2} radicals were made via two fluorescence assay by gas expansion (FAGE) detection cells.\textsuperscript{46} The limits of detection (LOD) on average for the campaign were 5.5 × 10\textsuperscript{3} molecules cm\textsuperscript{-3} for OH and 3.1 × 10\textsuperscript{6} molecules cm\textsuperscript{-3} for HO\textsubscript{2}. NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} were measured using a broadband cavity-enhanced absorption spectrometer (BBCEAS)\textsuperscript{47} with a conservative limit of detection of 1 ppt. The height of the boundary layer was measured by a ceilometer.\textsuperscript{48} Further information about the instrumentation can be found in the Supporting Information and in Shi et al.\textsuperscript{35} The campaign average diurnal profile of NO\textsubscript{3} is shown in Figure 1e and those of isoprene and OH are shown in Figure 2C.\textsuperscript{35,36} The meteorological variables of wind speed and direction, relative humidity, and temperature were measured at a height of 102 m on the IAP 325 m meteorological tower. Photolysis frequencies were calculated from the observed actinic flux using a spectral radiometer (Ocean Optics QE Pro spectrometer coupled to a 2nt sr actinic receiver optic (Meteorologie Consult GmbH)). The naming structure for IN species follows Schwantes et al.\textsuperscript{49} with the general structure INX, where the position of N is the first number given and X represents other functional groups on the molecule and its position is given by the second number.

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{2} concentrations and measurements of known NO\textsubscript{3} sinks,
including reaction with VOCs, photolysis, and loss via NO$_2$ 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 NO$_2$ production rates of the order of 4 ppbv h$^{-1}$, peaking in the late afternoon and early evening (Figure 1e). High daytime NO$_2$ loss rates, owing to rapid photolysis and reaction with NO, led to an average mixing ratio of ~2 pptv of NO$_2$ into the afternoon (Figure 1e). It is often assumed that daytime reactions of NO$_2$ 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 NO$_2$ loss mechanism during the day. Figure 1c shows the fractional loss of NO$_2$ calculated from measurements of various NO$_X$ sinks; the absolute loss rates are also shown in Figure S3. Reaction with NO and photolysis dominate the loss rate of NO$_2$ in Beijing. The mean NO$_2$ 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 (L$_{ISOP+OH}$ = k$_{OH}$ISOP[OH]) 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 NO$_X$ (L$_{ISOP+NOX}$ = k$_{NO}$NO[NO][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 O$_3$ was calculated to be a minor pathway, representing less than 10% of L$_{ISOP}$ throughout the day.

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

\[
P_{IN} = P_{IN} + P_{NO} = a_1 k_1 [OH ISOP] \tag{1} \\
P_{IN} + P_{NO} = a_2 k_2 [NO ISOP] \tag{2}
\]

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 × 10$^{-10}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ at 298 K) and NO$_X$ (6.5 × 10$^{-13}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ at 298 K), respectively. During the afternoon in Beijing, Newland et al. showed that the fraction of the peroxy (RO$_2$) radicals formed from isoprene + OH, reacting with NO can be as low as 65% (f$_{NO} = 0.65$), with the remainder reacting with RO$_2$, HO$_2$, 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. 2011.

\[
P_{IN} + P_{NO} = a_1 k_1 [OH ISOP] \times f_{NO} \tag{3}
\]

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/NO$_X$, the most recent IUPAC recommended value, and $a_2 = 0.76$ from isoprene + NO$_X$ from Schwantes et al. (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 O$_3$ is uncertain. The P$IN + P_{NO}$ was calculated following Liebmann et al. 2010 where the ozonolysis was assumed to lead to a 100% yield of RO$_2$ radicals and the OH ISN yield ($a_1 = 0.11$) was used. The total calculated ISN production rate (P$_{IN} + P_{NO} = P_{IN} + P_{NO} + P_{IN} + P_{NO}$) is shown in Figure 2B, with a maximum of 535 pptv h$^{-1}$ at 14:00. The relative contributions of the three pathways to P$_{IN} + P_{NO}$ are shown in Figure S6. O$_3$ represents a minor pathway of ISN production in Beijing during the measurements, with an average P$_{IN} + P_{NO}$ 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 NO$_X$ radical.

The calculated ISN production rates are shown in Figure 2B, with P$_{IN} + P_{NO}$ shown in red and P$_{IN} + P_{NO}$ shown in black. At midday, P$_{IN} + P_{NO}$ total is 480 pptv h$^{-1}$, with approximately 82% from the OH + NO chemistry (P$_{IN} + P_{NO}$) and 16% from NO$_X$ oxidation (P$_{IN} + P_{NO}$), as shown in Figure S6. The I-CIMS measured the sum of IHN (C$_2$H$_5$NO$_2$), 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. By 16:00, P$_{IN} + P_{NO}$ total dropped to ca. 210 pptv h$^{-1}$ as a result of the low NO$_X$ conditions in the afternoon and a reduction in the isoprene mixing ratios. At 16:00, 40% of the calculated P$_{IN} + P_{NO}$ total was from NO$_X$ + isoprene chemistry. Observations of δ-[1,4] and δ-[4,1]-isoprene carbonyl nitrates (INC) formed from NO$_X$ 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, they are present during the daytime in low concentrations indicating daytime production of ISN from isoprene + NO$_X$ chemistry. A similar trend is seen in C$_2$H$_5$NO$_2$ (black line in Figure 2D), which is likely to be a mixture of ISN produced from NO$_X$ chemistry (isoprene nitroxy hydroperoxide (INP), isoprene nitroxy hydroxyperoxide (INH), and isoprene dihydroxynitrile (IDHN)). 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.

<p>| 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$^a$ |
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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$^a$
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 isoprenederived mono-nitrated tracers (C\textsubscript{11}H\textsubscript{20}NO\textsubscript{5}S, molecular weight (MW) 261) and C\textsubscript{11}H\textsubscript{20}NO\textsubscript{5}S, MW 275) followed similar temporal trends as other OS and with a strong correlation with particulate sulfate as discussed below. 25 Four isoprenederived di-nitrated NOS isomers (C\textsubscript{11}H\textsubscript{19}NO\textsubscript{8}S, MW 306) and three tri-nitrated NOS isomers (C\textsubscript{11}H\textsubscript{18}NO\textsubscript{9}S, MW 351) were also observed, all showing a strong enhancement during the night.

Mono-nitrated NOS. A NOS (C\textsubscript{11}H\textsubscript{13}NO\textsubscript{5}S, MW 261) consistent with 2-methyltetrol nitroxyorganosulfate was observed, and the time series is shown in Figure 3a. This species had a mean concentration of 12.6 ng m\textsuperscript{-3}, a standard deviation of 19.6 ng m\textsuperscript{-3}, and a maximum of 154 ng m\textsuperscript{-3}. This mean concentration is similar to that of 2-methylglyceric acid (2MG) from isoprene + OH, as shown in Figure 3b. The NOS species had a strong enhancement during the night, 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 (R\textsuperscript{2} = 0.61) shown in Figure S7. This NOS species also correlated moderately to strongly with other OS species formed from isoprene oxidation by OH, as shown in Figure 3c–d. Two isoprenederived mono-nitrated NOS species formed may differ in their deviation of 26.3 ng m\textsuperscript{-3}.

Scheme 1. Proposed Formation Pathways of Mono-Nitroated OS and Di-Nitroanted OS Species Observed in the Aerosol from the NO\textsubscript{3} Initiated Oxidation of Isoprene\textsuperscript{a}

\begin{itemize}
  \item \textit{Note that only one of six possible INP isomers is shown, for simplicity, with \textit{δ}-[1,4]-INP and \textit{β}-[1,2]-INHE the dominant isomers observed in Schwantes et al.\textsuperscript{25}}
\end{itemize}

The reaction of isoprene with NO\textsubscript{3} radicals leads to isoprene nitrooxy peroxy radicals (INO\textsubscript{3}). Under the low concentrations of NO\textsubscript{3} observed in this study, NO\textsubscript{3} can react with HO\textsubscript{2}, leading to the formation of isoprene nitrooxy hydroperoxide (INO\textsubscript{3}P), as shown in the central section of Scheme 1. Using the observed concentrations of NO\textsubscript{3} and HO\textsubscript{2} measured, we estimated that up to 10–15% of INO\textsubscript{3}P can react with HO\textsubscript{2} during low NO afternoons in Beijing, as shown in Figure S8. There are six INP isomers possible and only the most abundant isomer (\textit{δ}-[1,4]-INP) observed by Schwantes et al.\textsuperscript{25} is shown. The reaction of INP with OH radicals, followed by OH recycling, can lead to INHE (\textit{β}-[4,1]-INHE and \textit{β}-[1,2]-INHE) in a similar way to the formation of isoprene-derived epoxidiols (IEPOX) from the reaction of OH with isoprene hydroxymethyloxirane (ISOPOOH).\textsuperscript{54} Schwantes et al.\textsuperscript{25} also showed that INHE could undergo reactive uptake to highly acidified aerosol, similar to IEPOX.

Figure 4. Box and whisker plots of observed NOS concentrations separated by the time of day the filter was collected: (A) C\textsubscript{11}H\textsubscript{13}NO\textsubscript{4}S, (B) C\textsubscript{11}H\textsubscript{14}NO\textsubscript{8}S, (C) C\textsubscript{11}H\textsubscript{19}NO\textsubscript{8}S, and (D) C\textsubscript{11}H\textsubscript{18}NO\textsubscript{9}S. The filter midpoints were split into different times of day, 00:00–07:00, 07:00–11:00, 11:00–13:00, and 13:00–17:00, based on the general sampling times of the filters (Table S2) and labeled as night, morning, midday, and afternoon, respectively. The thick black line represents the median value; the upper and lower hinges represent the 75th and 25th percentiles, respectively, with the upper and lower whiskers representing the largest value in the set. Outliers were removed so that the diurnal profiles could be seen more clearly.
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 (C₈H₁₀NO₃S, MW 306, with retention times 1.56, 1.86, 2.18, and 3.6 min) and three are tri-nitrate isomers (C₈H₁₀NO₄S, 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 + NO₂ 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 developed 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 NOS tracers have all previously been observed in chamber studies of NO₂ oxidation of isoprene.¹⁹,25,26 The same di-nitrates have also been observed during the oxidation of isoprene by OH in the presence of NO₂ but this is assumed to be a minor NOS formation pathway under the conditions observed in Beijing owing to their significant enhancement in the nighttime 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 hydroxynitrates (IHNs) from INO₂ + INO₂ self-reactions after the initial NO₂ attack. A second NO₂ 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 NO₂ reaction with isoprene leads to INO₂, and the reaction with HO₂ leads to the isoprene nitrooxy hydroperoxide (INP). Subsequent addition of a second NO₂ at the C₂ position of the remaining double bond leads to an alkyl radical on the C₂ position. This radical then eliminates OH to form isoprene di-nitrate epoxide (IDNE), as proposed in Kwan et al.²⁷ 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.,²³ the calculated OH production rate from this pathway during sunset and early evening (19:00–22:00) was relatively small, of the order of 2–5 x 10⁶ molecules cm⁻³ s⁻¹. The resulting IDNE species can then undergo heterogeneous uptake to acidic aerosols to form either di-hydroxy-di-nitrates 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 nighttime samples, suggesting their formation is a result of multiple steps of NO₂ oxidation. This is in contrast to the INHE-derived mono-nitrate outlined above that formed as a result of NO₂ oxidation followed by OH oxidation. The correlation of the di- and tri-nitrated NOS with particle sulfate is much weaker than the mono-nitrated NOS, as shown in Figure S7 (R² = 0.07–0.45). There is no correlation with the average night-time NO₂ mixing ratio (R² = 0.10), but there is a weak correlation with the maximum production rate of NO₂ (P(NO₂) = 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 NO₂ as shown in Figure 1e, resulting from lower levels of photolysis. The production will then reduce rapidly as the isoprene and NO₂ are consumed, with the mean NO₂ 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 NO₂ 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 short 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 nitrateg formation and act as a minor sink of atmospheric NO₂ 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.³¹ We suggest that the relatively high abundance of these species during the early morning sample may be the 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 NO₂ 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 NO₂ 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 nighttime NO₂ 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, NO₂, 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 NO₂ production and loss (Section S3); isoprene nitrate yields used in PlSnS calculations (Section S4); INO₂ reaction with H₂O⁺ and NO (Section S5); median diurnal variation of NO₂ loss fraction calculated using measured NO₂ sinks, including photolysis and
heterogeneous losses (Figure S1); calculated percentage of IN production (Figure S2); NO\textsubscript{3} loss rate calculated using measured NO\textsubscript{3} sinks (Figure S3); probability density function of the loss fraction of NO\textsubscript{3} (Figure S4); fractional NO\textsubscript{3} loss rate on the 14/06/2017, calculated using measured NO\textsubscript{3} sinks (Figure S5); fractional contribution to the calculated IN production rate (Figure S6); corplot 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{SOA}/(k\textsubscript{SOA} + k\textsubscript{NO\textsubscript{3}}) (Figure S8); average diurnal profile of boundary layer height (Figure S9); reactants 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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