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Impact of ozone and inlet design on the quantification of isoprene-derived organic nitrates by thermal dissociation cavity ring-down spectroscopy (TD-CRDS)

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Abstract. We present measurements of isoprene-derived organic nitrates (ISOP-NITs) generated in the reaction of isoprene with the nitrate radical (NO₃) in a 1 m^3 Teflon reaction chamber. Detection of ISOP-NITs is achieved via their thermal dissociation to nitrogen dioxide (NO2), which is monitored by cavity ring-down spectroscopy (TD-CRDS). Using thermal dissociation inlets (TDIs) made of quartz, the temperature-dependent dissociation profiles (thermograms) of ISOP-NITs measured in the presence of ozone (O_3) are broad (350 to 700 K), which contrasts the narrower profiles previously observed for, for example, isopropyl nitrate (iPN) or peroxy acetyl nitrate (PAN) under the same conditions. The shape of the thermograms varied with the TDI's surfaceto-volume ratio and with material of the inlet walls, providing clear evidence that ozone and quartz surfaces catalyse the dissociation of unsaturated organic nitrates leading to formation of NO₂ at temperatures well below 475 K, impeding the separate detection of alkyl nitrates (ANs) and peroxy nitrates (PNs). The use of a TDI consisting of a non-reactive material suppresses the conversion of isoprene-derived ANs at 473 K, thus allowing selective detection of PNs. The potential for interference by the thermolysis of nitric acid (HNO₃), nitrous acid (HONO) and O₃ is assessed.

1 Introduction

Understanding the atmospheric fate of nitrogen oxide (NO) and nitrogen dioxide (NO₂) is critical as both trace gases have a great impact on air quality and human health (Crutzen and Lelieveld, 2001; Lelieveld et al., 2015). Ambient mea-

surements of trace gases that function as NO_x reservoirs or sinks (where $NO_x = NO + NO_2$) are thus needed to provide insight into NO_x removal and transport. Organic compounds with nitrate functionality can serve as NO_x reservoirs in the troposphere (Thornton et al., 2002; Horowitz et al., 2007) and are generally categorized as peroxy nitrates (PNs, RO₂NO₂, with peroxy acetyl nitric anhydride (PAN) being its most abundant representative in the troposphere) and alkyl (aliphatic) nitrates (ANs, RONO₂). PNs are formed via the reaction of organic peroxy radicals (RO₂) with NO₂ (Reaction R1); ANs are formed via the minor (termolecular) channel of the reaction of RO₂ with NO (Reaction R2a). The competitive bimolecular process leads to alkoxy radicals (RO, Reaction R2b). During the daytime, RO₂ is formed mainly by the oxidation of volatile organic compounds (VOCs) by hydroxyl radicals (OH) in air (Reaction R3), with ozonolysis important at night (Reaction R4):

 $RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$ (R1)

$$RO_2 + NO + M \rightarrow RONO_2 + M$$
 (R2a)

 $\mathrm{RO}_2 + \mathrm{NO} \rightarrow \mathrm{RO} + \mathrm{NO}_2 \tag{R2b}$

$$VOC + OH(+O_2) \rightarrow RO_2 + products$$
 (R3)

$$VOC + O_3(+O_2) \rightarrow RO_2 + products.$$
 (R4)

At night-time, when OH radicals and NO are significantly less abundant, the NO₃ radical can initiate the oxidation of many VOCs that contain a double bond (Ng et al., 2017). NO₃, formed in the oxidation of NO₂ by O₃ (Reaction R5), is photolysed rapidly by sunlight (Reaction R6) and also reacts efficiently with NO (Reaction R7) so that it is generally of minor importance during the day (Wayne et al., 1991).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R5}$$

$$NO_3 + h\nu \to NO + O_2 \tag{R6}$$

$$NO_3 + NO \rightarrow 2NO_2$$
 (R7)

 NO_3 readily undergoes reactions with many unsaturated organic trace gases of biogenic origin including isoprene, monoterpenes and sesquiterpenes to form organic nitrates in high yields (Ng et al., 2017; Wennberg et al., 2018; Mellouki et al., 2021). The focus of this work is the formation of organic nitrates in its reaction (in air) with the C₅-diene isoprene (ISOP, Reaction R8):

$$NO_3 + ISOP(+O_2) \rightarrow \rightarrow ISOP-NIT,$$
 (R8)

where ISOP-NIT represents an isoprene-derived nitrate. Approximately 500 Tg yr⁻¹ of isoprene is released to the atmosphere (Guenther et al., 2012), and a large fraction of the organic nitrates formed at night-time is attributed to the reaction between NO₃ and isoprene (Reaction R8) (Carlton et al., 2009). The atmospheric oxidation of isoprene involving OH, O₃ and NO₃ as oxidizing agents is complex and leads to a huge variety of products (Ng et al., 2017; Wennberg et al., 2018) including multifunctional, unsaturated nitrates such as $O_2NOCH_2C(CH_3)=CHCH_2OH$ or $O_2NOCH_2C(CH_3)=CHCH_2OH$ or $O_2NOCH_2C(CH_3)=CHCH_2OH$ among other secondary oxidation products like dinitrates or epoxides (Wu et al., 2021).

Studies of the NO₃-induced oxidation of isoprene in air report AN yields between 60 % and 100 % (Barnes et al., 1990; Berndt and Boge, 1997; Perring et al., 2009; Kwan et al., 2012; Schwantes et al., 2015; IUPAC, 2021; Wu et al., 2021; Brownwood et al., 2021), and the NO₃-induced oxidation of isoprene is responsible for a dominant fraction of organic nitrates observed in rural environments with strong biogenic emissions (Beaver et al., 2012). The major fate of isoprene-derived organic nitrates formed in the boundary layer is deposition onto particulate matter to form nitric acid (HNO₃) or secondary organic aerosols (SOAs) leading to largely irreversible removal of NO_x from the gas phase (Ng et al., 2008; Rollins et al., 2009; Fry et al., 2018; Hamilton et al., 2021).

Individual isoprene nitrates have been measured selectively in the atmosphere by mass-spectrometric methods (Wolfe et al., 2007; Wu et al., 2021). An alternative detection scheme, in which the sum of all atmospheric PNs (Σ PNs) and ANs (Σ ANs) are separately measured, takes advantage of their different C–N bond energy by combining thermal dissociation to NO₂ (Reactions R9 and R10) with detection of the latter with means of laser-induced fluorescence (TD-LIF) or cavity ring-down spectroscopy (TD-CRDS).

$$\text{RO}_2\text{NO}_2 + \text{M} \rightarrow \text{RO}_2 + \text{NO}_2$$
 (R9)

 $RONO_2 + M \rightarrow RO + NO_2 \tag{R10}$

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Several instruments using thermal dissociation inlets consisting of fused silica (quartz) with residence times between tens to hundreds of milliseconds have been described in the literature (Day et al., 2002; Paul et al., 2009; Wild et al., 2014; Sobanski et al., 2016; Thieser et al., 2016; Keehan et al., 2020). In these instruments, quantitative conversion of PAN is reported for temperatures between 375 and 420 K. Generally, the temperature dependence of the instrument's response to ANs has been tested using mostly saturated organic nitrates such as isopropyl nitrate (iPN) and isobutyl nitrate, which are dissociated to NO₂ at temperatures between 500 and 675 K. The temperatures at which PNs and ANs are quantitatively converted to NO₂ thus differ by ~ 200 K and are largely independent of their organic backbone (Kirchner et al., 1999; Wild et al., 2014) allowing separate measurement of the sum of all alkyl nitrates (ΣANs) and of the sum of all peroxy nitrates (ΣPNs). These observations have provided the basis for analysis of field data in which an unknown mixture of PNs and ANs are present. We note, however, that most of the first-generation ANs formed in the NO₃ + isoprene system still contain a double bond (Barnes et al., 1990; Skov et al., 1992; Schwantes et al., 2015), which renders them more reactive towards oxidizing agents than, for example, iPN. A well-characterized thermogram for aliphatic nitrates derived from the oxidation of, for example, isoprene is thus a pre-requirement for extracting the mixing ratios of PNs and ANs from ambient measurements when using a TD inlet. To date, only one such thermogram has been presented (Brownwood et al., 2021) which appears to be the result of a single experiment (i.e. no variation of experimental conditions) using a sample that was not stable over time. The thermogram also features slopes before and after the AN transition temperature, which is consistent with the ideal behaviour of, for example, iPN.

In this study, we generated ISOP-NITs by reacting isoprene and NO₃ in a Teflon simulation chamber and used a custom-built, five-channel cavity ring-down spectrometer (CRDS) (Sobanski et al., 2016) to analyse the organic nitrates formed. In the presence of O₃ we find that ISOP-NIT does not behave like the saturated analogue iPN in our quartz TD inlet and we characterized the processes (both gas-phase and surface-catalysed processes) that lead to the observed behaviour. We also examined the potential role of surface-catalysed dissociation of HNO₃ and nitrous acid (HONO) to NO₂ as well as the effect of humidity as a potential bias to measurements of PNs and ANs.

2 Experiment

2.1 Simulation chamber

In order to analyse organic nitrates formed from the NO_3 + isoprene system under realistic operational conditions for the five-channel CRDS (e.g. normal sample flow

rates), we constructed a dynamic, flow-through simulation chamber "SCHARK" (Simulation CHamber for Atmospheric Reactions and Kinetics) of volume 1 m³ (cubic, all sides $\sim 1 \text{ m long}$) made of PFA foil of 0.005 in. ($\sim 0.13 \text{ mm}$) thickness (Ingeniven). The chamber is operated at ambient pressure and temperature; a magnetically coupled, Tefloncoated propeller-type stirrer situated in the centre of the chamber floor ensures continuous mixing of the air. The trace-gas inlets and sampling ports were located at opposite corners of the cubic chamber to reduce the potential of sampling gas that had not yet mixed. The PFA foil is surrounded by a $120 \times 120 \times 120$ cm cube constructed of four Perspex and two steel walls; the interspace (0.7 m³) is permanently flushed with 1 SLPM (L (STP) min⁻¹) of dry synthetic "zero air" in order to avoid contamination through permeation of trace gases present in the laboratory air. The Perspex walls serve as observation windows and were covered with lighttight material during the experiments described here.

Zero air was provided by passing pressurized air through a commercial air purifier (CAP 180, Fuhr GmbH). Humidification of the air was achieved with a permeation source (MH-110-24-F-4, Perma Pure LLC) filled with deionized water. Typical total flow rates of 15 or 23 SLPM zero air into the chamber result in exchange rates k_{exch} of 2.7 or $4.2 \times 10^{-4} \text{ s}^{-1}$, i.e. lifetimes of gases in the chamber of $\sim 40-60$ min. Note that in "flow-through" operation, the concentrations of trace gases in the chamber are controlled both by chemical processes and by the rate of flow into (and out of) the chamber so that "steady state" is achieved on the order of hours.

Ozone mixing ratios in SCHARK were measured by sampling 2 SLPM through a ~ 3 m long section of 0.25 in. (outer diameter, OD) PFA tubing to a commercial ozone monitor (2B Technologies, model 205) with a detection limit of ~ 1 part per billion by volume (ppbv) and 5% uncertainty. O₃ measurements were also used to establish the time required (under standard flow conditions) to achieve complete mixing within the chamber (< 1 min) and to derive the exchange rate by monitoring the exponential rise or decay of O₃ when its supply was switched on or off (Fig. S1 in the Supplement). O₃ (up to 600 ppbv) was generated by passing a fraction of the air flowing into the chamber through a UV-transparent cuvette (~70 cm³) illuminated by a low-pressure Hg lamp (PenRay) that dissociated O₂ (to O atoms and thus O₃) at 185 nm.

A known flow of isoprene entered the chamber as a dilute sample from a 12 L stainless-steel storage canister (Landefeld GmbH) which was prepared manometrically from evaporation of pure isoprene (Acros Organics, 98%) and mixed with helium (5.0, Westfalen). The isoprene concentration in the storage canister was quantified indirectly by measuring the NO₃ reactivity via flow-tube CRDS (Liebmann et al., 2017; Dewald et al., 2020) and was found to be 46.5 ppmv, in agreement (within 15%) with the manometrically derived mixing ratio. A gas sample of isopropyl nitrate (Sigma Aldrich, 58 ppmv in N_2 5.0, Westfalen) was prepared in a similar fashion.

Two methods of in situ NO₃ generation were employed. In the first, NO₃ was produced in the chamber via the reaction of NO₂ with O₃ (Reaction R5), whereby O₃ was generated as described above and NO₂ was taken from a bottled sample (Air Liquide, 1 ppmv in N₂). Typical concentrations of NO₂ and O₃ were 6–10 and 100–160 ppbv, respectively. Alternatively, NO₃ was generated in the thermal decomposition of N₂O₅ (Reaction R11) which was eluted into the chamber by passing a regulated flow of N₂ over N₂O₅ crystals held at temperatures between -78 and -70 °C.

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \tag{R11}$$

 N_2O_5 was synthesized by the sequential, gas-phase oxidation of NO (5% in N₂, Westfalen) in an excess of O₃ (Davidson et al., 1978) and trapped at -78 °C (acetone and dry ice). In this case, O₃ was obtained by electrical discharge through oxygen (5.0, Westfalen) using a commercial generator (Ozomat Com, Anseros). Note that the latter method enables us to generate NO₃ in the chamber in an O₃-free environment.

2.2 Detection of organic nitrates by cavity ring-down spectroscopy (CRDS)

Simultaneous measurements of the mixing ratios of NO₂, NO₃, N₂O₅, Σ ANs and Σ PNs in the SCHARK chamber were made using a five-channel cavity ring-down spectrometer (CRDS) that has been described in detail (Sobanski et al., 2016), and only a brief summary of key features of the instrument is given here. Each of the five cavities consists of FEP-coated (FEPD 121, DuPont) stainless-steel tubes which are equipped with two high-reflectivity mirrors (see below) supported 90 cm apart (*L*). The volumes in front of the mirrors are purged with dry synthetic air, which results in a reduction of the effective optical path length from 90 to 62.1 cm (*d*). The standard expression Eq. (1) is used to derive incavity concentrations [*X*] from the difference in ring-down constant in the absence (k_0) and presence (k) of an absorber *X*:

$$[X] = \frac{L}{d} \cdot \frac{1}{c\sigma_{\text{eff}}} \cdot (k - k_0), \qquad (1)$$

where *c* is the speed of light and σ_{eff} is the effective crosssection derived from the overlap of the laser emission and the NO₂ (Vandaele et al., 1998) or NO₃ absorption spectrum (Orphal et al., 2003).

Three of the cavities are operated at 409 nm for detection of NO₂, whereby 409 nm light is provided by a square-wavemodulated (2500 Hz) laser diode. The three 409 nm cavities, thermostated to 303 K and typically operated at a pressure of \sim 733 hPa, sampled from SCHARK at a total flow rate of 6 SLPM, which initially passes through a 2.3 m long PFA inlet (1.5 m with OD 0.25 in. and 0.8 m with OD 0.125 in.) before being split into three equal flows. One flow is directed to a cavity via an unheated, 60 cm long PFA tube (0.375 in. OD) to measure NO₂. The other two flows are directed through thermal dissociation inlets (TDIs) in which PNs and ANs are converted to NO₂. At the given conditions (i.e. flow rate, pressure, residence time in the heated section), keeping our TDI at temperatures close to 448 K results in quantitative conversion of PNs to NO₂ so that the cavity sampling via this inlet measures the sum of PNs + NO₂. Heating our second TDI to ≈ 650 K results in the complete conversion of ANs to NO₂ so that the sum of ANs + PNs + NO₂ can be measured as described in the literature cited in the introduction. The choice of material for these TD inlets has a profound influence on the results obtained, as described below.

The standard deviation (2σ) of consecutive baseline measurements defines the limits of detection (LODs), which are 38, 44 and 90 pptv for [NO₂], [Σ PNs] and [Σ ANs] respectively under laboratory conditions. The total uncertainty for the NO₂ measurement is 9%, which includes uncertainty in the (effective) NO₂ cross-sections. For the measurements of ANs and PNs the associated uncertainties are highly dependent on the concentrations of other trace gases and the corrective procedure accounting for radical recombination effects (Sobanski et al., 2016).

For simplicity, we refer to the three cavities as the "NO₂ cavity" (room-temperature inlet), the "PN cavity" (TD inlet at circa 473 K in which $\Sigma PNs + NO_2$ are measured) and the "AN cavity" (TD inlet at circa 673 K in which $\Sigma ANs + \Sigma PNs + NO_2$ are measured).

The remaining two cavities of the CRDS were operated at 662 nm (laser modulation at 625 Hz) for detection of NO₃. While one cavity is thermostated to 303 K (and detects NO₃ only), the second one (as well as an FEP-coated glass reactor located upstream) is thermostated to 373 K so that N₂O₅ is stoichiometrically converted NO3 and the summed mixing ratio of NO₃ and N₂O₅ is obtained. The two 662 nm cavities sampled air from SCHARK at a total flow rate of 15 SLPM through a \sim 1.5 m 1/4 in. (OD) PFA tube. Corrections to the mixing ratios were made to account for loss of NO₃ and N₂O₅ during transport to and through the cavities. Using the method described in Sobanski et al. (2016), NO3 transmission was found to be 89 % in both cavities. The NO₃ and N₂O₅ measurements are not central to this study but allowed the quantitative surveillance of NO₃ (and indirect N_2O_5) consumption by isoprene.

Figure 1 shows three types of thermal dissociation inlets (TDIs) used to convert organic nitrates to NO₂. In the original version of this instrument (Sobanski et al., 2016) the Σ PNs and Σ AN cavities sampled via 12 mm ID quartz TD inlets (TDI-1), with a length of 55 cm, the first ~ 10 cm of which was wrapped with heating wire. In order to reduce bias caused, for example, by the reformation of the organic nitrate after its thermal dissociation, this section was filled with glass beads (Sigma-Aldrich G9268, $\emptyset \sim 0.5$ mm) to provide a surface for heterogeneous loss of radicals. The glass beads were supported on a 2 cm thick glass frit and reduce the



Figure 1. Schematic diagram of the thermal dissociation inlets TDI-1, TDI-2 and TDI-3.

pressure downstream by \approx 28 hPa compared to TDI-1. Problems associated with temperature-dependent flow resistance through these small beads and the need for an extra filter (upstream) to prevent their transport into the inlet lines when flows were temporarily reversed (e.g. during instrument shutdown) led us to switch to larger beads (Merck, $\phi = 3 \text{ mm}$), and these were used throughout this study in TDI-1. TDI-2 is made of a quartz glass tube with the same dimensions as TDI-1 but features a longer heated section (20 cm) and is free of additional surfaces like glass beads or frits. TDI-2 is thus similar to many other thermal dissociation inlets described in the literature (see above). TDI-3 is constructed from a 55 cm long PFA tube (0.375 in. OD), where the first 20 cm is heated. The melting point of PFA is lower than the temperature required to thermally dissociate ANs, so TDI-3 could only be used for the measurement of $PNs + NO_2$. The temperature of the external wall of the TD inlets was measured with a K-type thermocouple situated at the centre of the heated section, which was insulated with mineral wool. At a flow rate of 2 SLPM and an operating pressure of 733 mbar, approximate residence times in the inlets without glass beads are 0.20 s (in TDI-2 at 650 K) and 0.13 s (TDI-3 at 450 K) when assuming a homogeneous temperature distribution equal to that measured on the outer wall of the tubing.

3 Results and discussion

Figure 2 shows the result of an experiment in which 150 sccm NO₂ (1 ppmv in air) was flowed into SCHARK along with isoprene (7 sccm of 46.5 ppmv in He) and 24 SLPM zero air of which 5 SLPM was passed over the low-pressure Hg-lamp zero air to generate O₃ (~96 ppbv). NO₂ was sampled (as usual) via the room-temperature PFA inlet, the Σ PNs (473 K) and Σ AN cavities (673 K) both sampled via TDI-1 (quartz tube with glass beads). O₃ was added at 09:30 and NO₂ at 10:00 (all times are local times, LT).

Just prior to the addition of isoprene at 12:00 LT, the system is close to steady state with ~ 5 ppbv NO₂ and 92 ppbv O₃. After subtraction of the measured N₂O₅ mixing ratios, a residual signal of ~ 100 pptv is detected in both the PN and AN channels, which may be caused, as discussed below, by interference of HNO₃ in the AN channel and a memory effect of the glass beads in the PN channel (Sect. 3.1 and 3.2). Note that after addition of isoprene, both NO₃ and N₂O₅ are reduced drastically (NO₃ ~ 3 pptv, N₂O₅ ~ 5 pptv) and the thermal dissociation of N₂O₅ no longer contributes to NO₂ signals in the PN and AN channels (Sobanski et al., 2016; Thieser et al., 2016).

At 14:00 LT, the cavity sampling from the 673 K TD inlet indicated $\sim 610 \,\text{pptv}$ for the summed mixing ratio of **CEI**(Σ ANs + Σ PNs), whereas the cavity sampling from the 473 K TD inlet (Σ PNs) indicated ~ 400 pptv. Since the signal in the Σ AN channel includes both the contribution of peroxy and alkyl nitrates, this implies that only 210 pptv (34%) of the detected products can be attributed to alkyl nitrates, which is inconsistent with the high yields (60 %-100 %) of ANs that result from the reaction of NO₃ with isoprene (Barnes et al., 1990; Berndt and Boge, 1997; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012; Schwantes et al., 2015; IUPAC, 2021; Brownwood et al., 2021). Compared to ANs, we expect the mixing ratios of, for example, PAN, $O_2NOCH_2C(CH_3)=CHC(O)O_2NO_2$ or methacryloyl peroxynitrate (MPAN) in this system to be negligible as their precursors such as O2NOCH2C(CH3)=CHCHO (Jenkin et al., 2015) or methacrolein (Kwok et al., 1996; Berndt and Boge, 1997; Schwantes et al., 2015) are oxidized only inefficiently in the dark. The formation of PNs only takes place once isoprene has been depleted so that secondary oxidation of the above-mentioned aldehydes by OH or NO₃ leading to further acyl-peroxy radicals (which form PNs) become at least competitive to the primary oxidation of isoprene. This is however never the case in the present experiments as isoprene is continuously flowed into the chamber and remains according to model calculations (see below) at a level of \approx 11.4 ppbv. Given the high abundance of O₃ and isoprene in this system, ozonolysis of the latter together with the associated formation and decomposition of Criegee intermediates to acetylperoxy radicals CH₃C(O)O₂ (Nguyen et al., 2016; Vansco et al., 2020) should make PAN the most important, potential contributor to a signal in the PN cavity. However, according to the branching ratios given in Nguyen et al. (2016), this reaction path is a minor one and $CH_3C(O)O_2$ (and thus PAN) should be formed in negligible amounts.

In order to identify the origin of the unexpectedly high Σ PN signal when NO₃ and isoprene are mixed in the dark, thermograms of the NO_3 + isoprene system were recorded in an experiment where ~ 2.8 ppbv of isoprene-derived nitrates (as measured with TDI-2 at 625 K) was generated by flowing NO₂ (200 sccm of 1 ppmv) and isoprene (9.8 sccm of 46.5 ppmv) in 15 SLPM dry synthetic air (with 5 SLPM over the Hg lamp for generation of $\sim 150 \text{ ppbv O}_3$). Similar to the experiment in Fig. 2, N₂O₅ mixing ratios are expected to be suppressed to a few parts per trillion by volume under these conditions so that its thermal dissociation (to NO₂) did not contribute to the Σ PN and Σ AN signals. Using this chemical system, we simultaneously measured ISOP-NIT thermograms once steady state established using TDI-1 (quartz, glass beads, 10 cm heated section) and TDI-2 (quartz, no glass beads, 20 cm heated section) both initially held at 703 K. Subsequently, both TDIs were cooled to ambient temperature over a period of \sim 1.75 h. The Σ AN signals from this experiment are plotted against the inlet temperature in Fig. 3a to generate the ISOP-NIT thermogram. This is displayed along with an isopropyl-nitrate thermogram (iPN, red data points) measured using the same inlets under the same flow conditions but using iPN diluted to 5.5 ppbv in dry synthetic air sampled directly through a PFA line (together with 1.5 ppby NO₂ impurity) to the instrument.

For iPN, we observe a well-defined onset of thermal dissociation at ~ 525 K with a plateau (maximum conversion) at ~ 650 K as reported previously for this set-up (Sobanski et al., 2016). When measuring iPN, TDI-1 results in a slightly steeper thermogram than TDI-2 in the 575–650 K range, which may be related to changes in gas flow and heat transfer within the inlet caused by the glass beads. Neither TD-inlet type results in dissociation to NO₂ at temperatures < 500 K. In contrast, the ISOP-NIT thermograms (normalized to the signal at the plateau at 625 K of TDI-2) indicate formation of NO₂ over a much broader range of temperatures (350–700 K).

The effect of humidifying the air was examined in an almost identical experiment conducted with NO₂ (150 sccm of 1 ppmv) and isoprene (7 sccm of 46.5 ppmv) in 15 SLPM synthetic air with relative humidity (in SCHARK) of 33.5 % at 22 °C. In this case, ~ 2.3 ppbv ISOP-NIT was formed. The thermograms obtained with TDI-1 and TDI-2 under these conditions are depicted in Fig. 3b. The broad thermogram measured with TDI-1 is very similar to that obtained under dry conditions (Fig. 3a), although even at room temperature an additional NO₂ signal of 500 pptv is detected. Sampling via TDI-2 yields an ISOP-NIT thermogram that has similar features to that obtained under dry conditions, although the peak at ~ 400 K has well-defined minima on both flanks and is shifted to higher temperatures. In separate experiments, humidified synthetic air (RH = 40 %, 23 °C) and

note the remarks at the end of the manuscript



Figure 2. Evolution of the mixing ratios of NO₂, Σ PNs, Σ PNs, Σ PNs, N_2O_5 and O₃ when flowing 150 sccm NO₂ (from 1 ppmv bottle), 7 sccm isoprene (from a 46.5 ppmv cylinder) and 24 SLPM of zero air (of which 5 SLPM was passed over a PenRay lamp) into SCHARK. Isoprene was added at 12:00 LT after the system was close to steady state. Note that the NO₂ and N₂O₅ mixing ratios were subtracted from the organic nitrate signals (**b**).

 NO_2 (10.8 ppbv) were sampled through a PFA line directly to the instrument. The thermogram (in the absence of isoprene or ISOP-NIT) using TDI-2 was recorded and can be found in the Supplement (Fig. S2) revealing that the presence of water and NO₂ in the inlet is sufficient to reproduce some features displayed in Fig. 3b with TDI-2. It is well known that H₂O and NO₂ can react on surfaces to form HONO and HNO₃ (Pitts et al., 1984; Finlayson-Pitts et al., 2003), and their formation in SCHARK was verified in Sect. 3.1. In the presence of H₂O, the efficiency of conversion of ISOP-NIT to NO₂ drops to about 5% at \sim 460 K. This is much less than under dry conditions whereby 20 % conversion of ISOP-NIT was observed between 375 and 475 K (Fig. 3a). Within a framework for surface-catalysed conversion of ISOP-NIT to NO₂ presented below, this observation can be interpreted as arising from the competitive adsorption to the surface of nitrated hydroperoxides and H₂O; i.e. H₂O (which is vastly more abundant) reduces the surface coverage of the organic nitrate at the surface.

The results in Figs. 2 and 3 show that separate detection of ANs and PNs based on their thermal dissociation can be problematic for the NO_3 + isoprene system. Identifying the cause of this and providing potential solutions to circumvent the problem is the aim of this work. To do this, we first focus on the "dry" experiment and highlight two regions of the

thermograms in which large deviations from the expected behaviour are observed.

3.1 Thermograms of ISOP-NIT

3.1.1 Region I (T > 648 K)

Figure 3a indicates that, at temperatures above 648 K (shaded region I), the behaviour of the two TDIs diverges significantly: while use of TDI-1 (glass beads) results in an increase in NO₂ with increasing temperature, the use of TDI-2 leads to a decrease in the NO₂ signal in the same temperature range. The increase in NO₂ continues at temperatures above that required to convert ANs to NO₂, which implies the presence of a NO₂-containing trace gas where the NO₂ moiety is more strongly bound than in ANs.

In order to assess to which extent this behaviour is potentially caused by inorganic trace gases that are not directly related to isoprene oxidation, an experiment with only NO₂ (2.75 ppbv) and O₃ (146 ppbv) in 23 SLPM dry synthetic air was performed. The steady-state concentration of N₂O₅ + NO₃ was measured as 78 pptv. The resulting thermograms using TDI-1 and TDI-2 and after subtraction of the signal from the NO₂ cavity (i.e. unheated inlet) are depicted in Fig. 4. No significant additional signal is observed



Figure 3. (a) Thermograms (relative to the signal at 650 K) of isoprene-derived organic nitrates (ISOP-NIT) and isopropyl nitrate (iPN) obtained with TDI-1 (solid symbols) and TDI-2 (open symbols) under dry conditions. (b) Absolute thermograms of ISOP-NIT obtained with TDI-1 (solid symbols) and TDI-2 (open symbols) under humid conditions (RH = 34 %, 22 °C). Regions (I and II) with unexpected detection of NO₂ are shaded yellow. Error bars denote standard deviation (1 σ , 30 s) of the signal.

below 475 K (region I) in either of the inlets. In region II (T > 675 K) on the other hand, we observed an increase (by ~ 500 pptv) in the signal at 703 K with TDI-1, whereas ~ 50 pptv is lost in TDI-2. In order to identify the trace gas(es) responsible for the signals observed in the system without isoprene, an iodide chemical ionization mass spectrometer (I-CIMS; Eger et al., 2019) described in the Supplement (Sect. S8) was coupled to the experiment. As shown in the Supplement (Fig. S3) both HNO₃ and nitrous acid (HONO) were observed as soon as O₃ and NO₂ were present in the chamber and their formation is enhanced in the pres-



Figure 4. Temperature-dependent NO₂ detection when sampling 2.75 ppbv NO₂ and 146 ppbv O₃ in 23 SLPM dry synthetic air from SCHARK through TDI-1 and TDI-2. The signal from the NO₂ cavity (no TDI) has been subtracted from both datasets. The mixing ratios of $N_2O_5 + NO_3$ (with associated uncertainty) are indicated by the blue area.

ence of water vapour, which is a common phenomenon in Teflon chambers (Pitts et al., 1984). We also found that reversing the flows and sampling the air into the CIMS *after* passing through the TDI-1 or TDI-2 (at 475 K) resulted in removal of the HNO₃. Sampling through TDI-1 also led to loss of HONO.

Various TD-CRDS and TD-LIF instruments report the detection of HNO₃ as NO₂ following thermal dissociation at temperatures around 700 K (Day et al., 2002; Wild et al., 2014; Thieser et al., 2016). The sensitivity of the present set-up to HNO₃ was investigated by sampling nitric acid from a calibrated permeation source (Friedrich et al., 2020) via TDI-1 and TDI-2 simultaneously. In these experiments, 22 ppbv HNO₃ (with 780 pptv NO₂ impurity) in dry synthetic air was delivered to the TDIs along with 350 ppbv O₃. The HNO₃ mixing ratio was derived using a known permeation rate (Friedrich et al., 2020) and dilution factor. Figure 5 shows the temperature-dependent conversion efficiency of HNO₃ to NO₂ in the presence of ozone (squares) with TDI-1 (black solid symbols) and TDI-2 (open symbols). Conversion of HNO₃ to NO₂ starts at \sim 550 K and increases with rising temperature. At 680 K, the conversion efficiency is 23 % for TDI-1 and 8 % for TDI-2. No significant conversion of HNO₃ to NO₂ was observed when ozone was absent (blue data points) and was drastically reduced when the synthetic air was humidified to RH = 55% at room temperature (red data points). The effect of water vapour is consistent with previous observations on the effect of humidity (Sobanski et al., 2016; Thieser et al., 2016; Friedrich et al., 2020).

The decomposition of HNO₃ to NO₂ thus only occurs in the presence of ozone under dry conditions, and its rate increases greatly at T > 650 K. This is consistent with the observations in Fig. 3b for TDI-1 and represents a likely



Figure 5. Thermograms of nitric acid (22 ppbv) in either dry (black) or humidified air (RH = 55 % at 23 °C, red) obtained with TDI-1 (closed squares) and TDI-2 (open squares). The O₃ mixing ratio was either zero or 350 ppbv in the non-humidified experiment and 350 ppbv in the humidified experiment. The error bars denote standard deviation (1 σ , 1 min) of the signal.

explanation for the increase in signal when sampling from SCHARK to investigate the NO₃ + isoprene system. The apparently more efficient (\sim factor three) conversion of HNO₃ to NO₂ in TDI-1 than in TDI-2 is explained by the loss of NO₂ at high temperatures in TDI-2 through the reaction with O atoms (see Sect. 3.2). In TDI-1 this is prevented by the removal of O atoms by the glass beads (e.g. via scavenging or surface-catalysed recombination to O₂).

The ozone-assisted conversion of HNO₃ to NO₂ cannot be explained by known gas-phase processes as the reaction between HNO₃ and O(³P) (Reaction R12) has a low rate coefficient ($k_{13} < 3 \times 10^{-17}$ cm³ molecule⁻¹s⁻¹ at 298 K; Burkholder et al., 2016) and results mainly in the formation of OH and NO₃ (Reaction R12). The more efficient conversion of HNO₃ to NO₂ in TDI-1 (with glass beads) compared to TDI-2 indicates that a surface-catalysed process involving either ozone or O(³P) is involved (Reaction R13).

$$HNO_3 + O(^{3}P) \rightarrow NO_3 + OH$$
 (R12)

$$HNO_3 + O_3 \text{ or } O(^{3}P) + \text{surface} \rightarrow NO_2 + \text{products}$$
 (R13)

Assuming that, in a Langmuir–Hinshelwood type process, the first step in the surface-catalysed reaction is physical adsorption of HNO₃ to the surface, the strong reduction in conversion of HNO₃ to NO₂ under humid conditions is explained by the competitive adsorption of HNO₃ and H₂O, the latter favoured by its much larger concentrations. That is, H₂O drives HNO₃ from the surface and thus protects it from surface reactions.

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3.1.2 Region II (T = 350-475 K)

In region II (350-475 K, shaded area in Fig. 3), instead of the near-zero signal expected in the absence of significant amounts of PNs or N₂O₅, we observe a monotonic increase in NO₂ with the temperature which is a factor of ~ 2 steeper in TDI-1 than in TDI-2. The signal in TDI-1 at 475 K, where only PNs are expected to dissociate, is $\sim 50 \%$ of the maximum signal at 650 K. There are several potential explanations for this behaviour, which include the following: (1) the formation and detection of thermally less stable ANs (e.g. including dinitrates), which dissociate at lower temperatures than, for example, iPN; (2) the formation of non-acyl, isoprene-derived peroxy nitrates (RO₂NO₂) that are sufficiently long-lived to build up to appreciable concentrations in SCHARK; and (3) chemical processes taking place in the TD inlets that convert ISOP-NIT to NO₂. Scenario (1) appears unlikely as several studies have shown that the O-N bond strength in various alkyl nitrates is very similar (Hao et al., 1994; Wild et al., 2014). We also note that the formation of dinitrates (in the absence of NO) only takes place when isoprene levels are very low and the first-generation nitrates formed in the NO₃ + isoprene reaction can react with a further NO₃. This can be ruled out for the present experiments in which the isoprene mixing ratio is always much larger than that of the first-generation nitrates formed, which in any case react much more slowly with NO₃ than does isoprene. The second explanation requires that RO₂ formed in the initial reaction between NO₃ and isoprene react with NO₂ to form RO₂NO₂. Given our experimental conditions, we would indeed expect that the main fate of any RO₂ formed in the reaction between NO₃ and isoprene is reaction with NO₂, which will dominate over self-reaction or reaction with NO₃, other RO₂ or HO₂. Non-acyl RO₂NO₂ are however generally highly thermally unstable, with lifetimes (at room temperature) of seconds or minutes, with respect to re-dissociation to $RO_2 + NO_2$.

For isoprene-derived RO_2NO_2 to contribute to the signal observed in region II would require that the RO_2-NO_2 bond strength be comparable to those of acyl nitrates such as PAN. The dominant 1,4-peroxy radical formed when NO_3 reacts with isoprene has a nitrate group separated by two carbon atoms from the peroxy carbon. It seems unlikely that this could have a stabilizing effect on the O–N bond in RO_2NO_2 in the same way that an α -carbonyl group does. Indeed, chamber experiments investigating the products of the NO_3 + isoprene reaction in detail (Barnes et al., 1990; Wu et al., 2021) have identified neither acyl- nor non-acyl- RO_2NO_2 as stable or semi-stable products formed from primary oxidation.

In support of scenario 3, Sect. 3.2 to 3.3 describe the evidence for chemical reactions leading to NO₂ formation that bypass the thermodynamic barrier for direct NO₂ formation but are surface-catalysed and require the presence of O₃ in either SCHARK or in the inlet. These processes are peculiar

to alkyl nitrates with a C=C double bond and thus have not been observed in TD inlets tested only with saturated alkyl nitrates such as the frequently used isopropyl nitrate.

3.2 The role of O₃

To further investigate the conversion of ISOP-NITs to NO_2 at low temperatures in the TD inlets, we generated NO_3 via the room-temperature thermal decomposition of N_2O_5 , thus ruling out chemical processes that were initiated or catalysed by O_3 .

In these experiments, N₂O₅ was transported into SCHARK by passing a flow of 0.1 SLPM dry synthetic air over a crystalline N₂O₅ sample cooled to -78 °C with further dilution in a 15 SLPM flow of zero air. The combined concentration of $N_2O_5 + NO_3$ that remains after the reaction with \sim 22 ppbv isoprene (7 sccm of 46.5 ppmv) was measured as 40.5 pptv. The use of high isoprene concentrations guarantees that the thermal decomposition of N_2O_5 does not contribute significantly to the thermograms. Under these conditions several parts per billion by volume of ISOP-NIT were formed. A constant flow (2 SLPM) of zero air was passed over a low-pressure Hg lamp and added between the sampling port of SCHARK and the inlets and TD inlets of the NO₂, PN and AN cavities. This way the O₃ mixing ratio in the TD inlets could be varied without affecting the chemistry in the chamber.

Figure 6 presents the results of one such experiment in which ISOP-NIT was sampled from SCHARK using TDI-1 and TDI-2, both initially held at 703 K with thermograms obtained by decreasing the temperature of both inlets in 25 K steps. At each temperature step (periods of 20 min), after recording the signal under O₃-free conditions (black squares), a low (40-54 ppbv, green triangles), medium (97-111 ppbv, blue triangles) and high (185–219 ppbv, orange circles) mixing ratio of O₃ was added in front of the TD inlets. Before cooling to the next temperature, the signal without O_3 was measured again and agreed within 30-150 pptv to the value at the beginning of the corresponding period. To enable comparison with "ideal" behaviour, the thermogram of isopropyl nitrate (iPN, red circles) recorded from an experiment while flowing 162 ppby O_3 (and 3 ppby NO_2 impurity) through SCHARK is also plotted.

Figure 6a displays a thermogram obtained when sampling ISOP-NITs from SCHARK via TDI-1 (glass beads). In the presence of O₃, the thermograms are very broad with substantial NO₂ formation between 350 and 475 K (shaded region II) and in this sense are comparable to those displayed in Fig. 3, where NO₃ was obtained from the reaction of NO₂ with O₃. In region I, the effect of going from ~ 50 to ~ 200 ppb of ozone is to increase the NO₂ generated drastically. This is the opposite of that observed when sampling via TDI-2 and thus in agreement with the results of the experiment depicted in Fig. 3, where the increase in signal was assigned to detection of HNO₃. For the experiments in which



Figure 6. (a) Thermograms of isoprene-derived nitrates generated by mixing N₂O₅ (as NO₃ source) and ~20 ppbv isoprene in SCHARK under dry conditions and sampling via TDI-1. The mixing ratio of O₃ (added only to the inlets) was varied from 0 to 202 ppbv. A thermogram of isopropyl nitrate (iPN) in the presence of 162 ppbv O₃ (and 3 ppbv NO₂ impurity) sampled through the same TDI is shown for comparison. The black solid line is a Boltzmann sigmoidal fit of the ozone-free experiment. The error bars show the standard deviation of the signal (1 σ). (b) Same as (a) but using TDI-2.

NO₃ was generated in the room-temperature thermal dissociation of N₂O₅, HNO₃ can arise from reactions of N₂O₅ with moisture on the walls and is present as impurity in the N₂O₅ sample. As described above, the presence of glass beads has two effects which operate in the same direction in this temperature regime: the conversion of HNO₃ to NO₂ is catalysed by the surface provided by the glass beads, and at the same time the loss of NO₂ (via reaction with O(³P)) is reduced as O(³P) is scavenged by the glass surface.

For TDI-1, the thermograms obtained without ozone (black squares) differ greatly to those in which ozone was present. Without ozone, NO₂ is not generated at temperatures lower than 550 K but its concentration increases rapidly at temperatures above ~ 600 K with no indication of a plateau being reached. The thermograms obtained in this NO₃-isoprene system using TDI-1 in the absence of ozone bear little resemblance to that of iPN. Furthermore, during pe-

riods without ozone or heat in TDI-1, compounds of lower volatility like ISOP-NITs or HNO3 appear to deposit on the glass beads and frit. This would form an explanation for a "memory effect" observed for TDI-1, whereby after exposure to HNO₃ or organic nitrates during unheated periods, an increase in the NO₂ signal followed by a slow decrease taking several hours is observed as soon as pure synthetic air and ozone were added to the flow through the heated inlet. An example of this phenomenon is shown in Fig. S4 in which (at peak signal) 60 ppbv of NO₂ was detected just by heating TDI-1 to 703 K in the presence of O₃ in synthetic air. In order to avoid bias in results caused by this effect, a cleaning procedure was adopted prior to all experiments whereby the inlet was heated to 703 K and exposed to ozone in synthetic air until a constant, low residual signal, usually between 20 and 200 pptv, was established. This memory effect seen for TDI-1 is also observed when a thermogram of ISOP-NIT (generated in a system similar to the experiment in Fig. 3) is measured by going from cold to hot temperatures (Fig. S5).

In Fig. 6b we present the results of the same experiment using TDI-2. The non-zero signal ($\sim 250 \text{ pptv}$) at temperatures between \sim 320 and 450 K) results from instability in the baseline. In the absence of ozone, the organic nitrates generated in the NO₃-initiated oxidation of isoprene follow a well-defined thermogram (black squares and solid line) between 475 and 650 K, which is very similar to the thermogram measured for iPN (red circles). The addition of ozone does not result in the formation of NO₂ in region II but does induce NO₂ losses for temperatures above 650 K (region I). The fact that ISOP-NIT was not converted to NO2 at temperatures < 475 K suggests that the observation of a large signal in Fig. 3a (region II, white squares) is linked to O₃-induced chemistry in SCHARK, which will be discussed in more detail in Sect. 3.3. The loss of NO₂ in region I increases with increasing amounts of O_3 with ~ 35 % of the NO₂ formed at 625 K lost when O₃ was increased to \sim 200 ppbv. The same behaviour is observed in the thermogram of iPN, which confirms that this process is independent of the nature of the nitrate but solely linked to thermal decomposition of O₃ and subsequent reactions of $O(^{3}P)$ with NO₂.

3.2.1 Thermal dissociation and gas-phase reactions of O₃ and O(³P)

An important clue to the underlying chemical processes that lead to the conversion of ANs to NO₂ at temperatures lower than those required to break the O–N bond is the fact that the thermogram of iPN (measured with TDI-1) is not significantly affected by the presence of 163 ppbv O₃, whereas thermograms of ISOP-NIT, the vast majority of which are unsaturated, are greatly broadened when O₃ is present.

It is well known that $O({}^{3}P)$ reacts rapidly (via electrophilic addition) to C=C double bonds (Leonori et al., 2015), and we thus assessed the potential impact of NO₂ formation via

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reactions of O_3 or $O({}^3P)$ (formed in the thermal dissociation of O_3 in the TDIs) with ISOP-NIT.

The concentration of $O({}^{3}P)$ in the TDIs depends on the concentration and rate of thermal decomposition of O_{3} and thus on the gas temperature as well as its rate of recombination with O_{2} , reactions with O_{3} , NO_{2} , isoprene, isoprene nitrates and loss to the walls:

$$O_3 + M \rightarrow O(^{3}P) + O_2 + M$$
(R14)

$$O(^{3}P) + O_{2} + M \to O_{3} + M$$
 (R15)

$$O(^{3}P) + O_{3} \rightarrow 2O_{2} \tag{R16}$$

$$O(^{3}P) + surface \rightarrow products$$
 (R17)

$$NO_2 + O(^{3}P) \rightarrow NO + O_2 \tag{R18}$$

$$ISOP-NIT + O_3 \rightarrow products + NO_2$$
(R19)

 $ISOP-NIT + O(^{3}P) \rightarrow products + NO_{2}$ (R20)

$$ISOP + O_3 \rightarrow products \tag{R21}$$

 $ISOP + O(^{3}P) \rightarrow products.$ (R22)

The contribution (in addition to the thermal dissociation of ISOP-NIT) to NO₂ formation via Reactions (R19) and (R20) in TDI-2 was assessed via numerical simulation (FAC-SIMILE/CHEKMAT release H010; Curtis and Sweetenham, 1987). The rate coefficients for the most important reactions are listed in Table 1; the complete reaction scheme is listed in the Supplement (Sect. S9). Reaction times in heated and unheated section of TDI-2 were calculated from the temperature, internal diameter of the quartz tube and the flow rate. The rate coefficients for the gas-phase reactions of isoprene (IUPAC, 2021) and 2-methyl-2-butene (Herron and Huie, 1973) with $O(^{3}P)$ and O_{3} were used as surrogates for the reactions of ISOP-NIT for which data are not available. The temperature-dependent dissociation rate coefficient of OP2npropyl nitrate was used to account for NO₂ from the thermal dissociation of isoprene-derived nitrates (Morin and Bedjanian, 2017). Wall loss of O(³P) in the instrument was estimated to be $90 \,\mathrm{s}^{-1}$ using the method as described in Thieser et al. (2016) and implemented in the model run.

The initial conditions for the simulation were 1 ppbv ISOP-NIT, 10 ppbv isoprene and 5 ppbv NO₂ at a cavity pressure of 724 hPa and a temperature of 298 K. The results obtained are shown by black curves in Fig. 7. For temperatures up to 575 K the simulated thermograms with and without O₃ are almost identical, whereas at higher temperatures, the amount of NO₂ exiting the inlet decreases because of its reaction with O(³P) (Reaction R17), in broad agreement with the experiments carried out using TDI-2 as shown in Fig. 3b. The model simulations show (Fig. 7) that almost no O(³P) is formed by the thermal dissociation of O₃ at the lower temperatures of region II. Only at higher temperatures is a significant fraction of O₃ (27 % at 703 K) converted to O(³P) with the majority subsequently lost at the inlet walls. These calculations underline the observation that the low temperature

Reaction	Rate constant	Reference
$ISOP-NIT + M \rightarrow RO + NO_2$	$3.16 \times 10^{15} \exp(-19676/T) \mathrm{s}^{-1}$	Morin and Bedjanian (2017)
$O_3 \rightarrow O(^3P) + O_2$	Pressure dependent (see text)	Peukert et al. (2013)
$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$	$6.0 \times 10^{-34} (T/300)^{-2.6} [M] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	IUPAC (2021)
$O(^{3}P) + O_{3} \rightarrow 2O_{2}$	$8.0 \times 10^{-12} \exp(-2060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	IUPAC (2021)
$O(^{3}P) + ISOP-NIT \rightarrow products + NO_{2}$	$3.9 \times 10^{-12} \exp(680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ a}$	Herron and Huie (1973)
$O(^{3}P) + ISOP \rightarrow products$	$3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (298 \text{ K})$	Paulson et al. (1995)
$O(^{3}P) + wall$	$90 \mathrm{s}^{-1}$	See text
$O(^{3}P) + NO_{2} \rightarrow NO + O_{2}$	$5.1 \times 10^{-12} \exp(198/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	IUPAC (2021)
$O_3 + ISOP \rightarrow products$	$1.05 \times 10^{-14} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	IUPAC (2021)
$O_3 + ISOP-NIT \rightarrow products + NO_2$	$1.05 \times 10^{-14} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ b}$	IUPAC (2021)

Table 1. Central reactions used for numerical simulation of the thermal dissociation of organic nitrates in TDI-2.

Notes: a value for 2-methyl-2-butene used. b Value for isoprene used.



Figure 7. Black lines and data points denote simulated, fractional conversion of n-propyl nitrate to NO₂ for TDI-2 without and with O₃ (200 ppbv). Red lines and data points denote simulated fractional conversion of O₃ to O(³P) within the heated section of TDI-2 with and without wall loss of O(³P). Error bars denote the standard deviation (1 σ) of the fractional conversion changing over time passed in the heated section.

formation of NO₂ from ISOP-NIT seen when using TDI-1 cannot be explained with known gas-phase chemistry.

In summary, the experimental observations and the numerical simulations indicate that the presence of O_3 is required in the inlet for TDI-1 and in the chamber for TDI-2 to generate NO₂ from isoprene-derived nitrates at temperatures less than 475 K. We have shown that the generation of NO₂ from alkyl nitrates at low temperatures using TDI-1 requires that the organic nitrate has a double bond and that, while gasphase reactions of O(³P) are responsible for the loss of NO₂ at high temperatures, they are *not* responsible for the conversion of isoprene-derived nitrates at lower temperatures in either of the TD inlets. The presence of glass beads (large surface area) favours the formation of NO₂ from ISOP-NIT at low temperatures. Altogether, these observations indicate that a surface-catalysed reaction involving ozone is the process most likely to be responsible for the conversion of ISOP-NIT to NO_2 at temperatures below those required for the gas-phase thermolysis.

3.2.2 Surface-catalysed reactions with ozone

Quartz tubes contain impurities and surface defects that can provide reactive sites (RSs) at elevated temperatures, and the surface-catalysed chemistry of ozone on, for example, mineral silicates is well known (Bulanin et al., 1994; Hanisch and Crowley, 2003a, b; Usher et al., 2003). O₃ can be surfacecatalytically converted to O₂ (Reaction R25) by the formation and loss of reactive, oxygenated surface sites (RSOs) via Reactions (R23) and (R24).

$RS + O_3 \rightarrow$	$RSO + O_2$	(R23))
			- /	

 $RSO + O_3 \rightarrow RS + 2O_2 \tag{R24}$

$$2O_3 \rightarrow 3O_2$$
 (R25)

In order to test for ozone loss in our set-up, O₃ in synthetic air was passed through the TDIs. The O₃ mixing ratio prior to entering the inlets was measured continuously using the ozone monitor (UV absorption). The ozone exiting the TD inlets was converted to NO₂ (by addition of 1 ppmv NO (Reaction R4) in a 1.5 m long PFA tubing with 0.5 in. OD and a residence time of 5.2 s) and then measured in the 409 nm cavities. Figure 8a shows the results of such an experiment for TDI-1. The concentration of ozone before entering the inlets was 20.5 ppbv (open dots), which was detected as 17.1 ppbv after passing through the inlet at 298 K (black squares, 11:15 to 11:55 LT). This represents a transition efficiency of 0.83, which matches that expected when considering the reaction time, NO concentration and the rate coefficient ($k_4 = 1.9 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, IUPAC, 2021).

At \approx 12:00 LT, upon heating the inlet to 473 K the ozone exiting TDI-1 was depleted by up to 27 %, while heating to



Figure 8. Time series of O_3 mixing ratios before and after passing though TDI-1 (a) or TDI-2 (b).

573 K results in further loss (up to 40%). An analogous experiment using TDI-2 (Fig. 8b) showed that while some O_3 was also lost (e.g. 4% at 573 K), this was much less than in TDI-1. As the gas-phase thermal decomposition of O_3 is negligible under these conditions (0.6% at 575 K, Fig. 7), the loss of O_3 when passing through the TD inlets indicates that surface-catalysed ozone decomposition takes place (Reactions R23 and R24), especially in TDI-1 where larger surface areas are available.

We now consider the possibility that the conversion of isoprene-derived nitrates to NO_2 can be catalysed by surfaces in the presence of O_3 . We note that previous work has shown that the heterogeneous ozonolysis of alkenes on glass or other surfaces can be more efficient than its analogous, gas-phase process (Dubowski et al., 2004; Stokes et al., 2008; Ray et al., 2013) and now consider the possibility that RSO is the mediating reactive species in TDI-1 in our experiments.

 $RSO + ISOP-NIT \rightarrow NO_2 + products$ (R26)

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We first examine the possible contributors to ISOP-NIT formed in the reaction of NO₃ with isoprene, in which the dominant initial step (in air) is a sequential 1,4 addition of NO₃ and O₂ to form δ - and β -peroxy radicals, e.g. O₂NOCH₂C(CH₃)=CHCH₂OO (Schwantes et al., 2015). In the presence of NO₃, RO₂ or HO₂, the peroxy radicals react further to form "first-generation" isoprene nitrates which contain carbonyl, hydroperoxidic and alcoholic groups such as O₂NOCH₂C(CH₃)=CHCHO, O₂NOCH₂C(CH₃)=CHCH₂OOH and O₂NOCH₂C(CH₃)=CHCH₂OH, respectively. Note that most of the known, first-generation organic nitrates retain a C=C double bond.

A hypothetical ISOP-NIT degradation scheme involving the initial attachment of RS-O to the remaining double bond is given in Fig. 9. We consider only the fate of the most stable surface adducts, i.e. tertiary radical in case of δ -products and secondary radicals in case of β -products. Both radical adducts will react with O₂ to form organic peroxy radicals which may undergo H shifts (via five- or six-membered rings) resulting in formation of a radical with its unpaired electron in the direct vicinity of the nitrate functionality. Such unimolecular processes may become competitive to bimolecular reactions under atmospheric conditions (Møller et al., 2019). A possible fate of this radical is decomposition to form a carbonyl compound via NO2 elimination (Hjorth et al., 1990; Berndt and Boge, 1995; Vereecken et al., 2021). For δ -products, the tertiary product may also eliminate NO₂ under the formation of an epoxide.

With TDI-2, the conversion of ISOP-NIT to NO₂ at low temperatures (region I) is only observed when O₃ is present in the chamber (Fig. 3a), but not when it is added only to the inlet (Fig. 6b) implying that the presence of O_3 as an oxidizing agent in SCHARK is the main difference between these two reaction systems. This suggests that the ozonolysis of isoprene may play an important role. As the reaction between isoprene and O₃ leads to the formation of OH and additional HO₂ (Zhang et al., 2002; Malkin et al., 2010; Cox et al., 2020), the fraction of RO₂ reacting with HO₂ in this system is enhanced when compared to the experiments in which NO₃ was generated from N₂O₅. The major product from the reaction between nitrated δ - and β -peroxy radicals with HO₂ is hydroperoxides, such as O₂NOCH₂C(CH₃)=CHCH₂OOH (Schwantes et al., 2015). With the intention of assessing the effect of O₃ on hydroperoxide yields, further model calculations were performed using the Framework for 0-D Atmospheric Modelling (F0AM) (Wolfe et al., 2016). The NO₃ isoprene oxidation scheme is still the subject of current research and uncertain, which is why the Master Chemical Mechanism (MCM, version 3.3.1, http://mcm.leeds.ac.uk, last access: 7 August 2021) (Jenkin et al., 2015) and the Reduced Caltech Isoprene Mechanism Plus (RCIMP, version 5, https://data.caltech.edu/records/247, last access: 7 August 2021) (Wennberg et al., 2018; Bates and Jacob, 2019) were applied. Figure 10 shows the calculated fraction of hy-



Figure 9. Possible mechanism for surface-catalysed conversion of first-generation ISOP-NIT in TDI-1. RS-O represents a reactive surface site.

droperoxides to ISOP-NIT using both models and mixing 22 ppbv isoprene with either 10.8 ppbv NO₂ and 150 ppbv O₃ (runs 1 and 3) or 3 ppbv N₂O₅ (runs 2 and 4) to achieve NO₃ in a flow-through chamber with an exchange rate of $2.73 \times 10^{-4} \,\mathrm{s}^{-1}$. Generally, the MCM predicts higher hydroperoxide yields than RCIMP. A possible reason might be that MCM has higher rates of HO₂ reformation from reactions of isoprene-derived alkoxy radicals than RCIMP does. For that reason, MCM only predicts an increase in the hydroperoxide yield by a factor of 1.33 when the NO₃ source is changed from N_2O_5 to $NO_2 + O_3$ (model runs 1 and 2), whereas RCIMP predicts a factor of 2.56 (model runs 3 and 4). The calculations thus broadly support the hypothesis that unsaturated, nitrated hydroperoxides are involved in the low temperature (surface-catalysed) formation of NO2 from ISOP-NIT. Indeed, hydroperoxides not only have high affinity for surfaces but also have a rather weak O-O bond with a dissociation energy of $\approx 45 \text{ kcal mol}^{-1}$ (Bach and Schlegel, 2020), and several routes to surface-catalysed elimination of NO₂ appear feasible. Decomposition of isoprene-derived hydroperoxides within the sampling line has been observed for other instruments (Rivera-Rios et al., 2014). A possible degradation mechanism for an isoprene-derived hydroperoxide which is abundant from the NO_3 + isoprene system (Schwantes et al., 2015) is depicted in Fig. 11. In this case, O2NOCH2C(CH3)=CHCH2OOH coordinates via hydrogen bonds to the SiO₂ surface prior to cleavage of the O-O bond to form OH and an alkoxy radical. The latter may dissociate via unimolecular reactions to form closed-shell products under elimination of NO₂ (Wennberg et al., 2018; Vereecken et al., 2021).



Figure 10. Simulated fractional contribution of hydroperoxy nitrates to ISOP-NIT using schemes taken from the MCM (red) and from RCIMP (black). The simulations reproduce the experimental conditions in Figs. 3 and 6, with 22 ppbv of isoprene together with either 3 ppbv N₂O₅ as NO₃ source (runs 1 and 3) or 10.8 ppbv NO₂ + 150 ppbv O₃ (runs 2 and 4).

3.3 Elimination of O₃ and surface-catalysed conversion of ANs at low temperatures

Our findings clearly show that the combination of heated quartz surfaces and ozone catalyse the decomposition of the unsaturated nitrates formed in the reaction between NO₃ and isoprene at temperatures below 473 K. While the exemplary, surface-catalysed processes depicted in Figs. 9 and 11 fulfil the requirement of conversion of ISOP-NIT to NO₂, we stress that these are purely hypothetical and we cannot state



Figure 11. Potential degradation pathways of isoprene-derived hydroperoxides on a heated quartz surface.

with any certainty that they are the reactions responsible for our observations. While it would be highly interesting to investigate such processes using different (e.g. surface sensitive) techniques, this is clearly beyond the scope of this paper and of the experimental capabilities of this research project. Instead, we take the more pragmatic approach and indicate potential methods to eliminate such unwanted reactions when using TD inlets.

In principal, as the processes that convert ISOP-NIT to NO₂ are clearly surface-catalysed (involving formation of RSO), their impact can be reduced by using a surface that does not support formation of RSO. We therefore tested a third TD inlet (TDI-3), consisting of 55 cm PFA tubing (0.375 in. OD) with a 20 cm heated section. PFA tubing has been routinely used as TDI for measurement of, for example, PAN, as it is relatively unreactive to the peroxy radicals formed (Phillips et al., 2013). The C-F bond of PFA is very strong and nonpolar, which should reduce the formation of RSO as well as adsorption of ISOP-NIT to the surface. The performance of a TDI made of PFA (TDI-3) was examined by performing an experiment with SCHARK analogous to the one shown in Fig. 2. The resulting time series of NO₂, Σ PNs (using TDI-3 heated to 448 K) and Σ ANs (using TDI-2 heated to 648 K) are depicted in Fig. 12. At first, O₃ (5 SLPM synthetic air passed over a Hg lamp) and NO₂ (200 sccm of 1 ppmv) in 25 SLPM dry synthetic air were constantly introduced into SCHARK. After detectable amounts of NO₃ and N₂O₅ had been formed, isoprene (9.8 sccm of 46.5 ppmv) was added leading (as expected) to almost quantitative depletion of NO₃ and N₂O₅.

During the following 3 h the signal in the Σ AN cavity (TDI-2) increased to ~ 1.2 ppbv, while the signal in the Σ PN channel (~ 40 pptv) was close to the detection limit. A CIMS measurement obtained during this experiment validates that PAN mixing ratios are lower than 50 pptv. This result already confirms that (1) the ANs derived from NO₃ + isoprene reac-

tion are not detected at T < 448 K when PFA is used instead of quartz and (2) as expected, there is no significant generation of peroxy nitrates in these experiments which would be detectable with both ovens at T = 448 K (see Fig. S6 in the Supplement).

This result not only confirms that the previous detection of ISOP-NITs at low TD-inlet temperatures when using TDI-2 and especially TDI-1 was caused by heterogeneous reactions at the quartz surface, but also provides a solution to the problem of the separate measurement of Σ ANs and Σ PNs using TD inlets.

We recall, however, that the reason for adding glass beads to the inlet was to suppress recombination reactions of NO₂ with peroxy radicals by providing a surface to scavenge the latter. The use of a PFA tube rather than quartz will certainly exacerbate this effect, as the rate of loss of RO₂ to PFA surfaces is expected to be lower than on quartz (Wooldridge et al., 2010). This implies that corrective procedures based on numerical simulation may be necessary in some environments as shown by Thieser et al. (2016), and this may limit the useful deployment of the method to regions where NO_x levels are sufficiently low that reaction of RO2 with NO and NO₂ become insignificant. In addition, similar to the observations of Sobanski et al. (2016), ClNO2 can interfere with the detection of ANs. The experiment shown in Fig. S7 reveals that ClNO₂ is detected with TDI-2 at 698 K, but not with TDI-3 at 448 K.

4 Summary, conclusions and implications for atmospheric measurements of ΣPNs and ΣANs

We have shown that the detection of isoprene-derived organic nitrates via its thermal dissociation in quartz/glass inlets can (in the presence of O_3) be accompanied by undesirable side reactions which broaden the thermograms and thus impede



Figure 12. Mixing ratios of NO₂, Σ PNs with TDI-3 and Σ PNs + Σ ANs with TDI-2 obtained from constant introduction of 200 sccm NO₂, and 9.8 sccm isoprene in 25 SLPM (of which 5 SLPM was passed over a PenRay lamp to generate O₃) dry synthetic air into SCHARK. A CIMS measurement of PAN is appended (blue squares).

the separation of PN and AN signals by sampling through TD inlets at different temperatures as is commonly practised. While our experiments deal with the nitrates formed in the NO₃-initiated oxidation of isoprene, it is very likely that similar broadening of thermograms would also occur with nitrates formed from the oxidation of other terpenoids, as some organic nitrates derived from night-time oxidation of, for example, limonene still contain a double bond (Fry et al., 2011) and/or contain hydroperoxy groups.

Specifically, we find that the presence of O_3 in either the quartz TD inlet or in a Teflon simulation chamber results in the generation of NO₂ from isoprene-derived nitrates in TD inlets made of quartz at temperatures less than 475 K and that this only occurs when the organic nitrate either has a double bond or a hydroperoxy group (or both). The formation of NO₂ from ISOP-NIT was accelerated in the presence of glass beads, which indicates that a surface-catalysed reaction involving ozone and reactive surface sites is the process most likely to be responsible both for the conversion of ISOP-NIT to NO₂ at low temperatures (375–475 K) and the conversion of HNO₃ to NO₂ at high temperatures (> 550 K). By avoiding the use of O₃ or using a non-quartz TD inlet, we were able to show that the ISOP-NIT thermogram is entirely consistent with those of saturated alkyl nitrates.

We show that surface-catalysed reactions on quartz TD inlets involving O₃ represent a potential source of bias in measurements of Σ ANs and Σ PNs during field observations, especially when isoprene is abundant. For example, we previously reported results from two campaigns carried out using the TD-CRDS system described here on the same rural mountain site (Kleiner Feldberg) and season (but in different years). We found that the average, relative abundance of Σ PNs and Σ ANs was quite different with Σ ANs $\approx \Sigma$ PNs during the PARADE campaign in 2011 and $\Sigma PNs > \Sigma ANs$ during the NOTOMO campaign in 2015 (Sobanski et al., 2017). In 2011, the TD inlet was a quartz tube (i.e. similar to TDI-2) (Thieser et al., 2016), whereas in 2015 the inlet contained glass beads (i.e. similar to TDI-1) (Sobanski et al., 2016). With our present understanding of the role of surfaces and O₃ in TD inlets, we cannot rule out that the observations during 2015 were biased to lower values for Σ ANs and higher values for Σ PNs, although, as discussed by Sobanski et al. (2017), there are other, meteorological factors which would have contributed.

For the detection of PNs we have shown that (at the lower temperature required to thermally dissociate PNs to NO_2) surface catalytic effects that convert ANs (or other species) to NO_2 can be completely avoided by using a TD inlet made of a non-reactive material like PFA (TDI-3). In this case, O_3 does not appear to have any impact.

When using a quartz TD inlet for conversion of ANs + PNs to NO_2 at higher temperatures, the surface re-

actions that shift thermograms to lower temperatures are of less significance as, in any case, the role of the TD inlet is to convert all ANs and all PNs to NO_2 . However, in order to avoid detection of HNO₃ or HONO other materials may be more suitable than quartz. Sapphire, commonly used in microwave discharge generated plasmas owing to its high purity and non-reactive surface, may represent a useful alternative. Under humid conditions, some of the observed interferences become negligible: HNO₃ appears not to interfere with the AN measurement, and the interference of ANs to the PN measurement is reduced in TDI-2, but not in TDI-1.

This study emphasizes the importance of characterizing thermal dissociation inlets under conditions which are similar to those found in the atmosphere. We recognize that the impact of surface catalytic processes will vary from one inlet to the next (even if made from the same material), and all quartz TDIs will not necessarily exhibit the same degree of conversion of biogenic VOC-derived ANs at low temperature. For this reason, thermograms should be measured using trace gases that are abundant in the atmosphere and the effect of, for example, O_3 and water vapour should be thoroughly investigated.

Data availability. The data underlying the figures are available on request from the corresponding author.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/amt-14-1-2021-supplement.

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