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Patrick Dewald, Jonathan Liebmann, Nils Friedrich, Justin Shenolikar, Jan Schuladen, et al.. Evolution of NO₃ reactivity during the oxidation of isoprene. *Atmospheric Chemistry and Physics*, 2020, 20 (17), pp.10459-10475. 10.5194/acp-20-10459-2020 . hal-02931874

HAL Id: hal-02931874

<https://hal.science/hal-02931874>

Submitted on 2 Nov 2020

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Evolution of NO₃ reactivity during the oxidation of isoprene

Patrick Dewald¹, Jonathan M. Liebmann¹, Nils Friedrich¹, Justin Shenolikar¹, Jan Schuladen¹, Franz Rohrer², David Reimer², Ralf Tillmann², Anna Novelli², Changmin Cho², Kangming Xu³, Rupert Holzinger³, François Bernard^{4,a}, Li Zhou⁴, Wahid Mellouki⁴, Steven S. Brown^{5,6}, Hendrik Fuchs², Jos Lelieveld¹, and John N. Crowley¹

¹Atmospheric Chemistry Department, Max-Planck-Institut für Chemie, 55128 Mainz, Germany

²Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany

³Institute for Marine and Atmospheric Research, IMAU, Utrecht University, Utrecht, the Netherlands

⁴Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS (UPR 3021)/OSUC, 1C Avenue de la Recherche Scientifique, 45071 Orléans CEDEX 2, France

⁵NOAA Chemical Sciences Laboratory, 325 Broadway, Boulder, CO 80305, USA

⁶Department of Chemistry, University of Colorado Boulder, Boulder, CO 80209, USA

^anow at: Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), Centre National de la Recherche Scientifique (CNRS), Université d'Orléans, Observatoire des Sciences de l'Univers en région Centre – Val de Loire (OSUC), Orléans, France

Correspondence: John N. Crowley (john.crowley@mpic.de)

Received: 16 April 2020 – Discussion started: 11 May 2020

Revised: 7 July 2020 – Accepted: 31 July 2020 – Published: 8 September 2020

Abstract. In a series of experiments in an atmospheric simulation chamber (SAPHIR,¹ Forschungszentrum Jülich, Germany), NO₃ reactivity (k^{NO_3}) resulting from the reaction of NO₃ with isoprene and stable trace gases formed as products was measured directly using a flow tube reactor coupled to a cavity ring-down spectrometer (FT-CRDS). The experiments were carried out in both dry and humid air with variation of the initial mixing ratios of ozone (50–100 ppbv), isoprene (3–22 ppbv) and NO₂ (5–30 ppbv). k^{NO_3} was in excellent agreement with values calculated from the isoprene mixing ratio and the rate coefficient for the reaction of NO₃ with isoprene. This result serves to confirm that the FT-CRDS returns accurate values of k^{NO_3} even at elevated NO₂ concentrations and to show that reactions of NO₃ with stable reaction products like non-radical organic nitrates do not contribute significantly to NO₃ reactivity during the oxidation of isoprene. A comparison of k^{NO_3} with NO₃ reactivities calculated from NO₃ mixing ratios and NO₃ production rates suggests that organic peroxy radicals and HO₂ account for ~ 50 % of NO₃ losses. This contradicts predictions based on numerical simulations using the Master Chemical Mechanism (MCM version 3.3.1) unless the rate coefficient for

reaction between NO₃ and isoprene-derived RO₂ is roughly doubled to $\sim 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

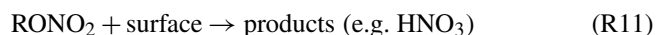
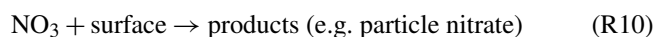
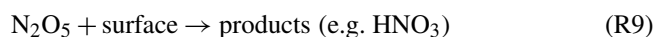
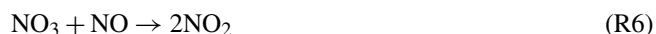
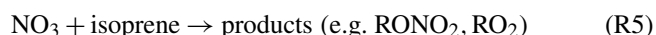
1 Introduction

The atmospheric oxidation of volatile organic compounds (VOCs) of both biogenic and anthropogenic origin has a great impact on tropospheric chemistry and global climate (Lelieveld et al., 2008). Isoprene is one of the major organic (non-methane) compounds that is released in the environment by vegetation and contributes ~ 50 % to the overall emission of VOCs into the atmosphere (Guenther et al., 2012). The most important initiators of oxidation for biogenic VOCs in the atmosphere are hydroxyl radicals (OH), ozone (O₃) and nitrate radicals (NO₃) (Geyer et al., 2001; Atkinson and Arey, 2003; Lelieveld et al., 2016; Wennberg et al., 2018). Our focus in this study is on NO₃, which is formed via the sequential oxidation of NO by ozone (Reactions R1 and R2). During the daytime, NO₃ mixing ratios are very low, owing to its efficient reaction with NO (Reaction R6) and its rapid photolysis (Reactions R7 and R8). Generally, NO₃ is present in mixing ratios greater than a few

¹Simulation of Atmospheric PHotochemistry In a large Reaction

parts per trillion by volume (pptv) only at night-time, when it can become the major oxidizing agent for VOCs including isoprene (Reaction R5). In forested regions, reactions with biogenic trace gases, however, can contribute significantly to the daytime reactivity of NO₃ (Liebmann et al., 2018a, b).

Moreover, NO₂, NO₃ and N₂O₅ exist in thermal equilibrium (Reactions R3 and R4) so that the heterogeneous loss of N₂O₅ (and NO₃) at surfaces (Reactions R9 and R10) impacts on the lifetime of NO₃ in the atmosphere (Martinez et al., 2000; Brown et al., 2003, 2006, 2009b; Crowley et al., 2010).



Although isoprene is mainly emitted by vegetation at daytime (Sharkey and Yeh, 2001; Guenther et al., 2012), during which its main sink reaction is with the OH radical (Paulot et al., 2012), it accumulates in the nocturnal boundary layer (Warneke et al., 2004; Brown et al., 2009a) where reactions of NO₃ and O₃ determine its lifetime (Wayne et al., 1991; Brown and Stutz, 2012; Wennberg et al., 2018). The rate constant (at 298 K) for the reaction between isoprene and NO₃ is $6.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is several orders of magnitude larger than for the reaction with O₃ ($1.28 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson et al., 2006; IUPAC, 2020) and thus compensating for the difference in mixing ratios of NO₃ (typically 1–100 pptv) and O₃ (typically 20–80 ppbv) (Edwards et al., 2017). NO₃ is often the most important nocturnal oxidant of biogenic VOCs (Mogensen et al., 2015), especially in remote, forested environments where it reacts almost exclusively with biogenic isoprene and terpenes (Ng et al., 2017; Liebmann et al., 2018a, b). The reaction between isoprene and NO₃ leads initially to the formation of nitro isoprene peroxy radicals (NISOPPOO, e.g. O₂NOCH₂C(CH₃)=CHCH₂OO) that can either react with NO₃, forming mostly a nitro isoprene aldehyde (NC4CHO, e.g. O₂NOCH₂C(CH₃)=CHCHO) and methyl vinyl ketone (MVK) or react further with other organic peroxy (RO₂), or hydroperoxy (HO₂) radicals, forming nitrated carbonyls, peroxides and alcohols (Schwantes et al., 2015).

The organic nitrates formed (RONO₂) can deposit on particles (Reaction R11); therefore, the NO₃ + isoprene system contributes to the formation of secondary organic aerosol

(SOA) (Rollins et al., 2009; Fry et al., 2018). Together with heterogeneous uptake of N₂O₅ or NO₃ on particle surfaces (Reactions R9 and R10), the build-up of SOA from isoprene oxidation products forms a significant pathway for removal of reactive nitrogen species (NO_x) from the gas phase; a detailed understanding of the reaction between isoprene and NO₃ is therefore crucial for assessing its impact on SOA formation and NO_x lifetimes.

In this study, the NO₃-induced oxidation of isoprene was examined in an environmental chamber equipped with a large suite of instruments, including a cavity ring-down spectrometer coupled to a flow tube reactor (FT-CRDS) for direct NO₃ reactivity measurement (Liebmann et al., 2017). The NO₃ lifetime in steady state (the inverse of its overall reactivity) has often been derived from NO₃ mixing ratios and production rates, with the latter depending on the mixing ratios of NO₂ and O₃ (Heintz et al., 1996; Geyer and Platt, 2002; Brown et al., 2004; Sobanski et al., 2016b). The steady-state approach works only if NO₃ is present at sufficiently high mixing ratios to be measured (generally not the case during daytime), breaks down to a varying extent if a steady state is not achieved (Brown et al., 2003; Sobanski et al., 2016b), and may be influenced by heterogeneous losses of NO₃ or N₂O₅ (Crowley et al., 2011; Phillips et al., 2016), which are difficult to constrain. Comparing the steady-state calculations with the FT-CRDS approach (which derives the NO₃ reactivity attributable exclusively to VOCs) can provide insight into the main contributions to NO₃ reactivity and its evolution as the reaction progresses. In the following, we present the results of direct NO₃ reactivity measurements in the SAPHIR (Simulation of Atmospheric Photochemistry In a large Reaction) environmental chamber under controlled conditions and explore the contributions of isoprene, peroxy radicals and stable oxidation products to NO₃ reactivity over a period of several hours as the chemical system resulting from NO₃-induced oxidation of isoprene evolves.

2 Measurement and instrumentation

An intensive study of the NO₃ + isoprene system (NO₃ISOP campaign) took place at the SAPHIR chamber of the Forschungszentrum Jülich over a 3-week period in August 2018. The aim of NO₃ISOP was to improve our understanding of product formation in the reaction between NO₃ and isoprene as well as its impact on the formation of SOA. Depending on the conditions (high or low HO₂/RO₂, temperature, humidity, and daytime or night-time), a large variety of oxidation products, formed via different reaction paths, exist (Wennberg et al., 2018). During NO₃ISOP, the impact of varying experimental conditions on the formation of gas-phase products as well as secondary organic aerosol formation and composition was explored within 22 different experiments (see Table 1). Typical conditions were close to those found in the atmosphere with 5 ppbv of NO₂, 50–100 ppbv of

O₃ and 3 ppbv of isoprene, or (when high product formation rates were required) NO₂ was raised to 25 ppbv and isoprene to 10 ppbv. The high O₃ mixing ratios in the chamber ensured that NO was not detectable (< 10 pptv) in the darkened chamber.

The first 11 experiments of NO₃ISOP were dedicated to gas-phase chemistry; in the second part seed aerosol ((NH₄)₂SO₄) was added and the focus shifted to aerosol measurements. Due to a contamination event in the chamber, the experiment from the 7 August is not considered for further analysis. The SAPHIR chamber and the measurements and instruments that are relevant for the present analysis are described briefly below.

2.1 The SAPHIR chamber

The atmospheric simulation chamber SAPHIR has been described in detail on various occasions (Rohrer et al., 2005; Bossmeyer et al., 2006; Fuchs et al., 2010), and we present only a brief description of some important features here: the outdoor chamber consists of two layers of FEP (fluorinated ethylene propylene) foil defining a cylindrical shape with a volume of 270 m³ and a surface area of 320 m². The chamber is operated at ambient temperature and its pressure is ~ 30 Pa above ambient level. A shutter system in the roof enables the chamber to be completely darkened or illuminated with natural sunlight. Two fans result in rapid (2 min) mixing of the gases in the chamber, which was flushed with synthetic air (obtained from mixing high-purity nitrogen and oxygen) at a rate of 250 m³ h⁻¹ for several hours between each experiment. Leakages and air consumption by instruments leads to a dilution rate of typically $1.4 \times 10^{-5} \text{ s}^{-1}$. Coupling to a separate plant chamber enabled the introduction of plant emissions into the main chamber (Hohaus et al., 2016).

2.2 NO₃ reactivity measurements: FT-CRDS

The FT-CRDS instrument for directly measuring NO₃ reactivity (k^{NO_3}) has been described in detail (Liebmann et al., 2017) and only a brief summary is given here. NO₃ radicals are generated by sequential oxidation of NO with O₃ (Reactions R1 and R2) in a darkened, thermostated glass reactor at a pressure of 1.3 bar. The reactor surfaces are coated with Teflon (DuPont, FEPD 121) to reduce the loss of NO₃ and N₂O₅ at the surface during the ~ 5 min residence time. The gas mixture exiting the reactor (400 sccm) is heated to 140 °C before being mixed with either zero air or ambient air (at room temperature) and enters the FEP-coated flow tube where further NO₃ production (Reaction R2), equilibrium reaction with N₂O₅ (Reactions R3 and R4), and NO₃ loss via reactions with VOCs/NO (Reactions R5/R6) or with the reactor wall (Reaction R10) take place. NO₃ surviving the flow reactor after a residence time of 10.5 s is quantified by CRDS at a wavelength of 662 nm. The NO₃ reactivity is calculated from relative change in NO₃ concentration when mixed with

zero air or ambient air. In order to remove a potential bias by ambient NO₃/N₂O₅, sampled air is passed through an uncoated 2 L glass flask (~ 60 s residence time) heated to 45 °C to favour N₂O₅ decomposition before reaching the flow tube. Ambient NO₃ (or other radicals, e.g. RO₂) is lost by its reaction with the glass walls. In addition to the reaction of interest (Reaction R5), Reactions (R2) to (R4) and (R10) affect the measured NO₃ concentration so that corrections via numerical simulation of this set of reactions are necessary to extract k^{NO_3} from the measured change in NO₃ concentration, necessitating accurate measurement of O₃, NO and especially NO₂ mixing ratios. For this reason, the experimental setup was equipped with a second cavity for the measurement of NO₂ at 405 nm as described recently (Liebmann et al., 2018b). In its current state the instrument's detection limit is ~ 0.005 s⁻¹. By diluting highly reactive ambient air with synthetic air, ambient reactivities up to 45 s⁻¹ can be measured. The overall uncertainty in k^{NO_3} results from instability of the NO₃ source and the CRDS detection of NO₃ and NO₂ as well as uncertainty introduced by the numerical simulations. Under laboratory conditions, measurement errors result in an uncertainty of 16 %. The uncertainty associated with the numerical simulation was estimated by Liebmann et al. (2017), who used evaluated rate coefficients and associated uncertainties (IUPAC), to show that the uncertainty in k^{NO_3} is highly dependent on the ratio between the NO₂ mixing ratio and the measured reactivity. If a reactivity of 0.046 s⁻¹ (e.g. from 3 ppbv of isoprene) is measured at 5 ppbv of NO₂ (typical for this campaign), the correction derived from the simulation would contribute an uncertainty of 32 % to the resulting overall uncertainty of 36 %. For an experiment with 25 ppbv of NO₂ and 10 ppbv of isoprene, large uncertainties (> 100 %) are associated with the correction procedure as the NO₃ loss caused by reaction with NO₂ exceeds VOC-induced losses. Later we show that data obtained even under unfavourable conditions (high NO₂ mixing ratios) are in accord with isoprene measurements, which suggests that the recommended uncertainties in rate coefficients for Reactions (R3) and (R4) are overly conservative.

The sampled air was typically mixed with ~ 50 pptv of NO₃ radicals, and the reaction between NO₃ and RO₂ radicals generated in the flow tube (Reaction R5) represents a potential bias to the measurement of k^{NO_3} . In a typical experiment (e.g. 3 ppbv of isoprene), the reactivity of NO₃ towards isoprene is 0.046 s⁻¹. A simple calculation shows that a total of 20 pptv of RO₂ radicals has been formed after 10.5 s reaction between NO₃ and isoprene in the flow tube. Assuming a rate coefficient of ~ $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction between NO₃ and RO₂, we calculate a 5 % contribution of RO₂ radicals to NO₃ loss. In reality, this value represents a very conservative upper limit as RO₂ is present at lower concentrations throughout most of the flow tube, and its concentration will be significantly reduced by losses to the reactor wall and self-reaction. In our further analysis we therefore do not consider this reaction.

Table 1. Experimental conditions in the SAPHIR chamber during the NO₃ISOP campaign.

Date	<i>T</i> (°C)	H ₂ O (%)	D/N	O ₃ (ppbv)	NO ₂ (ppbv)	Isoprene (ppbv)	Seed aerosol	Notes
31 July	25–35	0	N	90–120	1–5	0	–	
1 August	22–31	0	N	85–115	2–5	1.2	–	
2 August	23–38	0	N	85–120	2–5	2.5	–	
3 August	30–42	1.3–2.7	D → N	45–100	1–5	2.5	–	
6 August	20–44	1.4	N → D	40–110	1–6	3.2	–	
7 August	20–41	0.45–0.6	N	45–60	3–4.5	2.3	–	contamination
8 August	22–28	0	N	75–115	13–30	8	–	
9 August	20–27	0	N	65–115	6–2.5	3	–	CO and propene
10 August	17–28	0	N	40–65	3–5.5	1.8	–	
12 August	14–36	0	N → D	70–115	4–12	3	–	CO
13 August	28–24	0	N	75–110	12–23	6	–	
14 August	18–24	0	N	70–110	13–22	13	(NH ₄) ₂ SO ₄	reduced fan operation
15 August	20–28	1.3–2	N	80–115	8–21	9	(NH ₄) ₂ SO ₄	
16 August	20–28	1.6	N → D	80–115	2–5	3	(NH ₄) ₂ SO ₄	
17 August	18–26	1.2–1.7	N → D	0–400	0–17	0	–	isobutyl nitrate, calibration
18 August	14–31	1.3–1.4	N → D	80–110	2–5	3.5	(NH ₄) ₂ SO ₄	β-caryophyllene
19 August	16–31	0.07	N	0–110	0–20	3	(NH ₄) ₂ SO ₄	MVK, N ₂ O ₅ as NO ₂ source
20 August	20–26	1.2–19	N	85–130	3–5	6	(NH ₄) ₂ SO ₄	β-caryophyllene
21 August	20–30	1.5–1.9	N	55–130	2–5	4.5	(NH ₄) ₂ SO ₄	CO and propene
22 August	18–33	1.3–17	N	75–110	2.5–8.5	5	(NH ₄) ₂ SO ₄	plant emissions
23 August	18–31	1.5–2.2	N	45–100	3.5–5	4	(NH ₄) ₂ SO ₄	
24 August	17–23	1–1.6	N	85–110	2.3–5.5	22	NH ₄ HSO ₄	β-caryophyllene

D/N denotes if the experiment was conducted with the chamber roof opened (D: daytime) or closed (N: night-time) and in which order a transition was done. Only maximum values of measured isoprene are listed.

2.3 VOC measurements: PTR-ToF-MS

During the NO₃ISOP campaign, isoprene and other VOCs were measured by two different PTR-ToF-MS (proton transfer reaction time-of-flight mass spectrometer) instruments. The PTR-TOF1000 (IONICON Analytic GmbH) has a mass resolution $> 1500 m/\Delta m$ and a limit of detection of < 10 ppt for a 1 min integration time. The instrumental background was determined every hour by pulling the sample air through a heated tube (350 °C) filled with a Pt catalyst for 10 min. Data processing was done using PTRwid (Holzinger, 2015), and the quantification and calibration was done once per day, following the procedure as described recently (Holzinger et al., 2019).

The Vocus PTR (Tofwerk AG and Aerodyne Research Inc.) features a newly designed focusing ion–molecule reactor, resulting in a resolving power of $12\,000 m/\Delta m$ (Krechmer et al., 2018). Calibration was performed on an hourly basis for 5 min. The isoprene measurements of the two instruments agreed mostly within the uncertainties (14 %). An exemplary comparison between the two instruments of an isoprene measurement can be found in the Supplement (Fig. S1). For the evaluation of the experiment on the 2 August, only data from the PTR-TOF1000 were available. For all the other experiments of the campaign, isoprene and

monoterpene mixing ratios were taken from the Vocus PTR, owing to its higher resolution and data coverage.

2.4 NO₃, N₂O₅, NO₂, NO, and O₃ measurements

The NO₃/N₂O₅ mixing ratios used for analysis are from a harmonized data set including the measurements from two CRDS instruments. Data availability, quality and consistency with the expected NO₃/N₂O₅/NO₂ equilibrium ratios were criteria for selecting which data set to use for each experiment. Both instruments measure NO₃ (and N₂O₅ after its thermal decomposition to NO₃ in a heated channel) using cavity ring-down spectroscopy at a wavelength of ~ 662 nm. The 5-channel device operated by the Max Planck Institute (MPI) additionally measured NO₂ and has been described recently in detail (Sobanski et al., 2016a). Its NO₃ channel has a limit of detection (LOD) of 1.5 pptv (total uncertainty of 25 %); the N₂O₅ channel has a LOD of 3.5 pptv (total uncertainty of 28 % for mixing ratios between 50 and 500 pptv). Air was subsampled from a bypass flow drawing ~ 40 SLPM through a 4 m length of 0.5 in. (inner diameter, i.d.) PFA (perfluoroalkoxy alkane) tubing from the chamber. Variation of the bypass flow rate was used to assess losses of NO₃ (< 10 %) in transport to the instrument, for which correction was applied. Air entering the instrument was passed through a Teflon membrane filter (Pall Corp., 47 mm, 0.2 µm pore), which was changed every 60 min. Corrections for loss

of NO₃ and N₂O₅ on the filter and inlet lines were carried out as described previously (Sobanski et al., 2016a).

The second CRDS was built by the NOAA Chemical Sciences Laboratory (Dubé et al., 2006; Fuchs et al., 2008, 2012; Wagner et al., 2011; Dorn et al., 2013) and operated by the Institut de Combustion, Aérodynamique, Réactivité et Environnement (ICARE). During the NO₃ISOP campaign, the NOAA-CRDS was positioned beneath the chamber, and air was sampled through an individual port in the floor. The sampling flow rate was 5.5–7 L min⁻¹ through a Teflon FEP line (i.d. 1.5 mm, total length about 0.9 m) extending by about 50 cm (i.d. 4 mm) with 25 cm (i.d. 4 mm) in the chamber. A Teflon filter (25 µm thickness, 47 mm diameter, 1–2 µm pore size) was placed downstream of the inlet to remove aerosol particles and changed automatically at an interval of 1.5–2 h, depending on the conditions of the experiments, such as the amount of aerosol in the chamber. The instrument was operated with a noise equivalent 1σ detection limit of 0.25 and 0.9 pptv in 1 s for the NO₃ and N₂O₅ channels, respectively. The total uncertainties (1σ) of the NOAA-CRDS instrument were 25 % (NO₃) and −8 %/+11 % (N₂O₅).

NO₂ mixing ratios were taken from a harmonized data set combining the measurements of the 5-channel CRDS with that of the NO₃ reactivity setup as well as the NO_x measurement of a thermal dissociation CRDS setup (Thieser et al., 2016). The NO_x measurement could be considered a NO₂ measurement since during dark periods of the experiments NO would have been present at extremely low levels. The total uncertainty associated with the NO₂ mixing ratios is 9 %.

NO was measured with a LOD of 4 pptv via chemiluminescence (CL; Ridley et al., 1992) detection (ECO Physics, model TR780), and ozone was quantified with a LOD of 1 ppbv by ultraviolet absorption spectroscopy at 254 nm (Ansyco, ozone analyser 41M). Both instruments operate with an accuracy (1σ) of 5 %.

2.5 Box model

The results of the chamber experiments were analysed using a box model based on the oxidation of isoprene by NO₃, OH and O₃ as incorporated in the Master Chemical Mechanism (MCM), version 3.3.1 (Saunders et al., 2003; Jenkin et al., 2015). In this work, the analysis focusses on the fate of the NO₃ radical, so the oxidation of some minor products was omitted in order to reduce computation time. Moreover, the most recently recommended rate coefficient (IUPAC, 2020) for the reaction between NO₃ and isoprene ($k_5 = 2.95 \times 10^{-12} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was used instead of the value found in the MCM v3.3.1, which is 6.8 % higher. Chamber-specific parameters such as temperature and pressure as well as the time of injection and amount of trace gases added (usually O₃, NO₂ and isoprene) were the only constraints to the model. The chamber dilution flow was implemented as first-order loss rates for all trace gases and wall loss rates for NO₃ or N₂O₅ were introduced (see

Sect. 3.2). The numerical simulations were performed with FACSIMILE/CHEKMAT (release H010, date 28 April 1987, version 1) at 1 min time resolution (Curtis and Sweetenham, 1987). The chemical scheme used is listed in the Supplement (Table S1).

3 Results and discussion

An overview of the experimental conditions (e.g. isoprene, NO₃, NO₂ and O₃ mixing ratios) on each day of the campaign is given in Fig. 1. The temperature in the chamber was typically between 20 and 30 °C but increased up to 40 °C when the chamber was opened to sunlight. The relative humidity was close to 0 % during most of the experiments before 14 August. After this date, the experiments focussed on secondary organic aerosol formation and humidified air was used.

We divide the experiments into two broad categories according to the initial conditions: type 1 experiments were undertaken with NO₃ production from 5 ppbv of NO₂ and 100 ppbv of O₃. The addition of isoprene with mixing ratios of ∼ 3 ppbv resulted in NO₃ reactivities of around 0.05 s⁻¹ at the time of injection. The NO₃ and N₂O₅ mixing ratios were typically of the order of several tens of parts per trillion by volume (pptv) in the presence of isoprene under dry conditions. During humid experiments (with seed aerosol), NO₃ mixing ratios were mostly below the LOD in the presence of isoprene, owing to increased uptake of NO₃/N₂O₅ on particles. An exceptionally large isoprene injection (∼ 20 ppbv) resulted in the maximum NO₃ reactivity of 0.4 s⁻¹ on the 24 August. In type 2 experiments, higher NO₃ production rates were achieved by using 25 ppbv of NO₂ and 100 ppbv of O₃. In these experiments, with the goal of generating high concentrations of organic oxidation products, isoprene mixing ratios of 10 ppbv resulted in reactivities of ∼ 0.2 s⁻¹ at the time of isoprene injection. Owing to high NO₃ production rates, several hundred parts per trillion of NO₃ and a few parts per billion of N₂O₅ were present in the chamber.

Figure 1 shows that once isoprene has been fully removed at the end of each experiment, the NO₃ reactivity tends towards its LOD of 0.005 s⁻¹, indicating that the evolution of the NO₃ reactivity is closely linked to the changing isoprene mixing ratio.

3.1 Comparison of k^{NO_3} with calculated reactivity based on measurements of VOCs

The VOC contribution to the NO₃ reactivity is the summed first-order loss rate coefficient attributed to all non-radical VOCs present in the chamber that can be transported to the FT-CRDS according to Eq. (1):

$$k^{\text{NO}_3} = \sum k_i [\text{VOC}]_i, \quad (1)$$

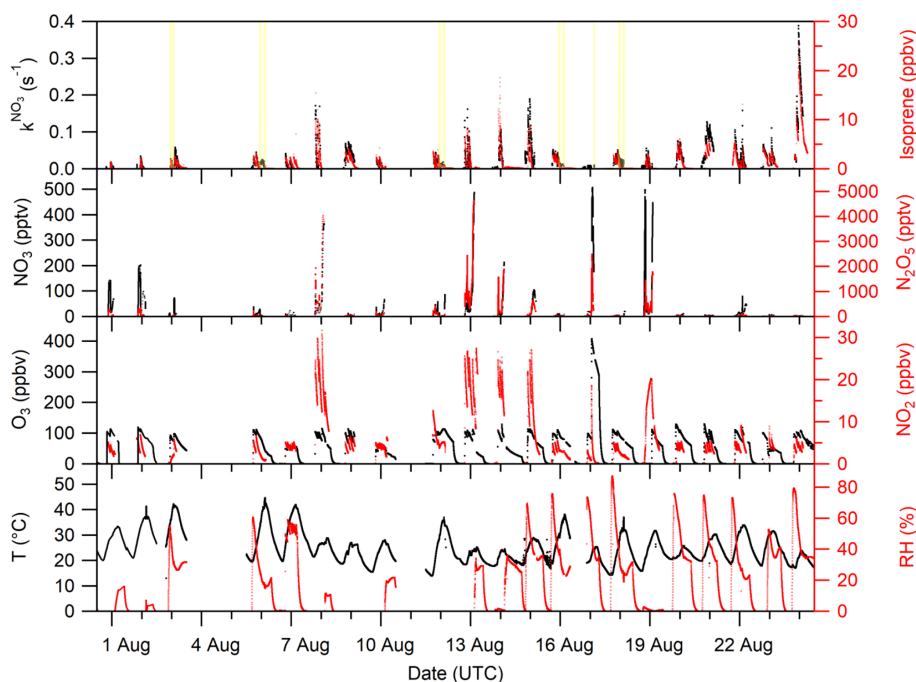


Figure 1. Overview of the temperature (T); relative humidity (RH); VOC-induced NO₃ reactivity (k^{NO_3}); and the O₃, NO₂, NO₃, N₂O₅, and isoprene mixing ratios during the NO₃ISOP campaign. The yellow shaded area in the upper panel represent phases of the experiment when the chamber roof was opened. The ticks mark 12:00 UTC of the corresponding day.

where k_i is the rate coefficient ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction between a VOC of concentration $[\text{VOC}]_i$ and NO₃.

Reliable values of k^{NO_3} and VOC data are available from the 2 August onwards (see Table 1 for experimental conditions) and were used to compare FT-CRDS measurements of k^{NO_3} with $\Sigma k_i[\text{VOC}]_i$. For most of the experiments, isoprene was the only VOC initially present in the chamber, and at the beginning of the experiments k^{NO_3} should be given by $k_5[\text{isoprene}]$, with the latter measured by the PTR-MS instruments (see above). On the 9 and 21 August, both isoprene and propene (100 ppbv) were injected into the chamber; the summed NO₃ reactivity from these trace gases was then $k_5[\text{isoprene}] + k_{\text{propene}}[\text{propene}]$, with $k_{\text{propene}} = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, 2020). As no propene data were available, the propene mixing ratios were assessed with the model (see above) based on injected amounts as well as subsequent loss by oxidation chemistry (mainly ozonolysis) and dilution. On the 22 August, coupling to a plant emission chamber permitted the introduction of monoterpenes and isoprene into the main chamber so that the NO₃ reactivity was $k_5[\text{isoprene}] + k_{\text{monoterpenes}}[\text{monoterpenes}]$. The uncertainty in $\Sigma k_i[\text{VOC}]_i$ was propagated from the standard deviation of the isoprene and monoterpene mixing ratios and from the uncertainties of 41 % in k_5 , 58 % in k_{propene} (IUPAC, 2020) and 47 % in $k_{\text{monoterpenes}}$ (average uncertainty of three dominant terpenes; see below).

Figure 2a depicts an exemplary time series of k^{NO_3} and $\Sigma k_i[\text{VOC}]_i$ between the 9 and 13 August. The measured k^{NO_3} and values of $\Sigma k_i[\text{VOC}]_i$ calculated from measured isoprene (and modelled propene in the case of the 9 August) are, within experimental uncertainty, equivalent, indicating that the NO₃ reactivity can be attributed entirely to its reaction with isoprene (and other reactive trace gases like propene) injected into the chamber.

The correlation between k^{NO_3} and $\Sigma k_i[\text{VOC}]_i$ for the entire campaign data set is illustrated in Fig. 2b. Type 2 experiments (high NO₂ mixing ratios) were included despite the unfavourable conditions for measurement of k^{NO_3} , which result in large correction factors via numerical simulation (see above). The data points obtained on the 14 August display large variability, which is likely to have been caused by non-operation of the fans leading to poor mixing in the chamber. An unweighted linear regression of the whole data set yields a slope of 0.962 ± 0.003 , indicating excellent agreement between the directly measured NO₃ and those calculated from Eq. (1). The intercept of $(0.0023 \pm 0.0004) \text{ s}^{-1}$ is below the LOD of the reactivity measurement. A correlation coefficient of 0.95 underlines the linearity of the whole data set despite increased scatter caused by the unfavourable conditions during type 2 experiments. Note that data from the 7 August (chamber contamination) were not used. On the 15 and 21 August, additional flushing of the chamber with synthetic air (150–300 m³) and humidification shortly before the actual beginning of the experiment resulted in a constant back-

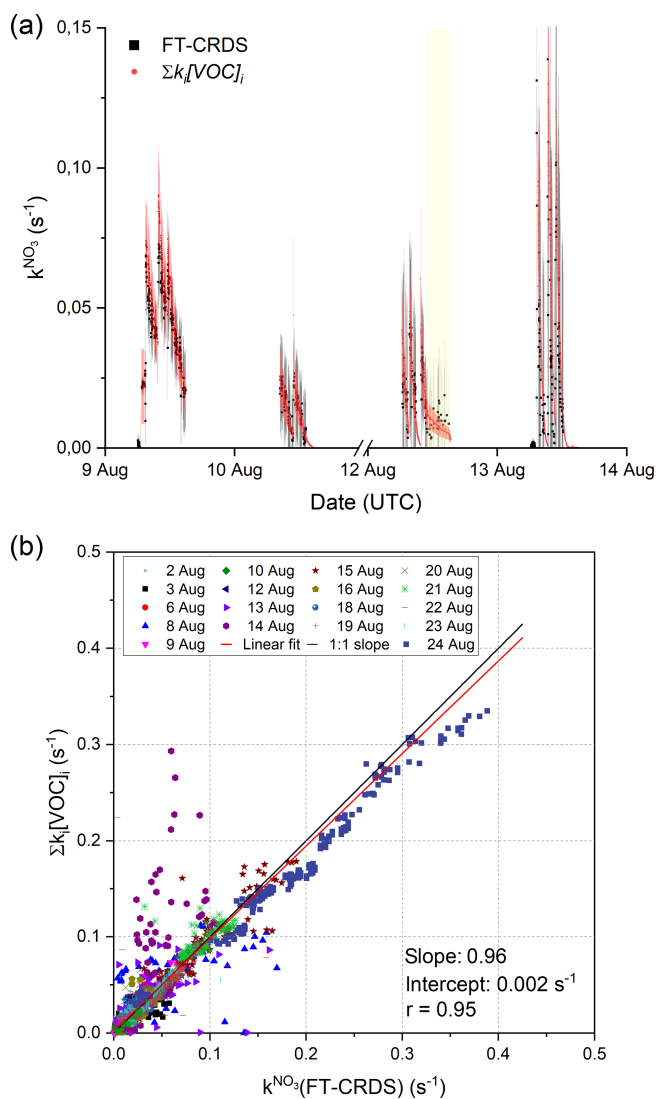


Figure 2. (a) 4 d time series of k^{NO_3} and $\Sigma k_i[\text{VOC}]_i$. The total uncertainty in k^{NO_3} was calculated as described by Liebmann et al. (2017) and is indicated by the grey shaded area. The red shaded area shows the associated uncertainty of the calculated reactivities and are derived from error propagation using the standard deviation of the isoprene mixing ratios and an uncertainty of 41 % for the rate coefficient for reaction between NO₃ and isoprene (IUPAC, 2020). The ticks mark 00:00 UTC of the corresponding date, and yellow shaded areas represent periods in which the chamber roof was opened. (b) Correlation between $\Sigma k_i[\text{VOC}]_i$ and k^{NO_3} measurements. The red line represents a least-squares linear fit to the entire data set, while the black line illustrates an ideal slope of 1 : 1.

ground reactivity in k^{NO_3} of 0.04 s⁻¹ on the 15 August and 0.012 s⁻¹ on the 21 August. High background reactivity was not observed during other humid experiments if the chamber was flushed extensively with synthetic air ($\sim 2000 \text{ m}^3$) during the night between experiments and if the additional flushing was omitted. The trace gas(es) causing this background reactivity could not be identified with the available measure-

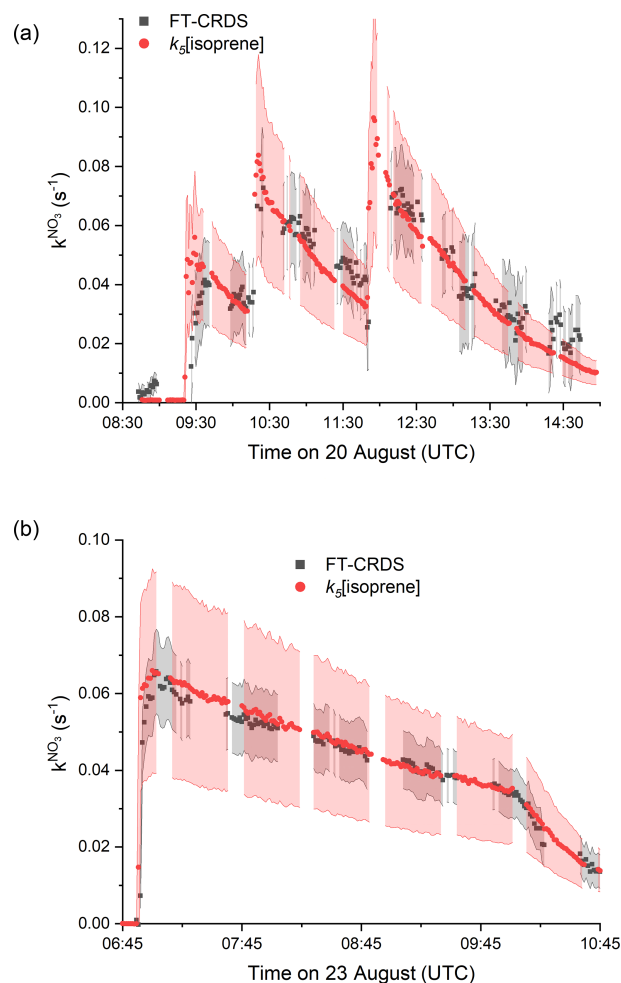


Figure 3. Measured reactivity (k^{NO_3} , black data points) and reactivity calculated from Eq. (1) (red data points), which is equivalent to $k_5[\text{isoprene}]$. The grey shaded area represents the total uncertainty in k^{NO_3} ; the red shaded areas represent the total uncertainty in $k_5[\text{isoprene}]$ and were estimated as explained in Fig. 2. (a) 20 August: type 1 experiment with initial mixing ratios of NO₂ = 4.6 ppbv and O₃ = 120 ppbv. (b) 23 August: only O₃ (100 ppbv) and isoprene (4 ppbv) were initially present.

ments, but they are probably released from the chamber walls during flushing and humidification. In order to make a detailed comparison with the VOC data, the background reactivity, which was fairly constant, was simply added.

A more detailed examination of k^{NO_3} data from two type 1 experiments (low NO₂) is given in Fig. 3. The grey shaded areas indicate the total uncertainty associated with the FT-CRDS measurement of k^{NO_3} (Liebmann et al., 2017); the scatter in the data stems mostly from the correction procedure via numerical simulation.

On the 20 August (Fig. 3a), in addition to NO₂ and O₃, (NH₄)₂SO₄ seed aerosol ($\sim 50 \mu\text{g cm}^{-3}$) and β -caryophyllene (~ 2 ppbv) were injected at 08:40 UTC in order to favour formation of secondary organic aerosol. The

instrument was zeroing until shortly after the injection of this terpene. As the lifetime of β -caryophyllene is extremely short in the chamber under the given conditions (~ 150 s), only the small fraction of unreacted β -caryophyllene contributes to the k^{NO_3} signal observed after 08:40 UTC. At 09:20, 10:13 and 11:50 UTC isoprene was injected into the chamber, resulting in step-like increases in the measured NO₃ reactivity. Each increase in reactivity and the ensuing evolution over time match well with the calculated values of $k_5[\text{isoprene}]$ (red data points). The red shaded area indicates the overall uncertainty in the latter. Clearly, within experimental uncertainty, the NO₃ reactivity is driven almost entirely by reaction with isoprene, with negligible contribution from stable, secondary products.

During the experiment of the 23 August (Fig. 3b), only isoprene and ozone were present in the chamber for the first 4 h. Isoprene depletion is dominated by ozonolysis at this phase, whereas the sudden drop in k^{NO_3} is caused by an increased dilution flow during humidification of the chamber around 10:00 UTC. The absence of NO₂ results in a more accurate, less scattered measurement of k^{NO_3} and underscores the reliability of the measurement under favourable conditions. All of the observed reactivity can be assigned to isoprene that was injected at 06:52 UTC. This implies that stable secondary oxidation products from isoprene ozonolysis (such as formaldehyde, MACR (methacrolein), MVK) are insignificant for k^{NO_3} , which is consistent with the low rate coefficients (e.g. $k_{\text{MACR}+\text{NO}_3} = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as highest of the three; IUPAC, 2020).

The results of a type 2 experiment with NO₂ mixing ratios of ~ 20 ppbv as well as higher isoprene mixing ratios (injections of ~ 8 and ~ 3 ppbv under dry conditions) are depicted in Fig. 4a. Despite the requirement of large correction factors to k^{NO_3} owing to the high NO₂ to isoprene ratios, fair agreement between measured k^{NO_3} and the expected reactivity is observed for each of the isoprene injections at 07:30, 09:20 and 10:50 UTC. The agreement may indicate that the uncertainty in k^{NO_3} (grey shaded area), which is based on uncertainty in, for example, the rate coefficient for reaction between NO₃ and NO₂ (Liebmann et al., 2017), is overestimated.

In Fig. 4b we display the results of an experiment on 12 August, in which the initially darkened chamber (first ~ 4 h) was opened to sunlight (final 4 h). NO₂ mixing ratios varied between 12 and 4 ppbv and isoprene was injected (~ 3 ppbv) three times at 05:55, 07:40 and 09:45 UTC. During the dark phase, measured k^{NO_3} follows $k_5[\text{isoprene}]$. At 11:00 UTC the chamber was opened to sunlight, during which approximately 5 ppbv of NO₂, 200–150 pptv of NO and < 1 ppbv of isoprene were present in the chamber. In this phase, the loss of NO₃ was dominated by its photolysis and reaction with NO. Within experimental uncertainty, the measured daytime k^{NO_3} after correction for both NO₂ and NO (correction factors between 0.05 and 0.02) during the sunlit period was still close to $k_5[\text{isoprene}]$.

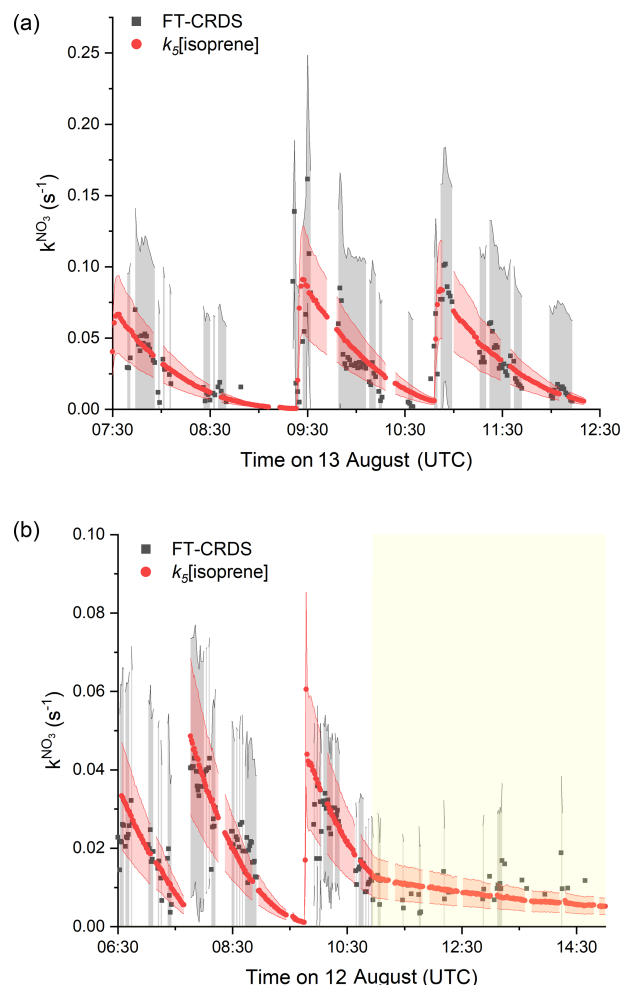


Figure 4. Measured (black) and expected (red) NO₃ reactivity using Eq. (1). The corresponding uncertainties were estimated as described in Fig. 2 and are indicated as shaded areas. **(a)** Type 2 experiment is from the 13 August under dry conditions with initial mixing ratios of NO₂ = 25 ppbv and O₃ = 104 ppbv. **(b)** Experiment from the 12 August is with NO₂ mixing ratios between 7 and 12 ppbv and initial mixing ratio of O₃ = 79 ppbv. The yellow shaded area denotes the period with the chamber roof opened after 11:00 UTC.

On the 22 August, the SAPHIR chamber was filled with air from a plant chamber (SAPHIR-PLUS) containing six European oaks (*Quercus robur*) which emit predominantly isoprene but also monoterpenes, mainly limonene, 3-carene and α -pinene (van Meeningen et al., 2016).

The time series of measured NO₃ reactivity (k^{NO_3} , black data points) after coupling to the plant chamber at 08:00 UTC is shown in Fig. 5. Data after 11:40 UTC are not considered, because the chamber lost its pressure after several recoupling attempts to the plant chamber. Also plotted (red data points) is the NO₃ reactivity calculated from $\sum k_i[\text{VOC}]_i$, whereby both isoprene and the total terpene mixing ratio (up to 500 pptv) were measured by the Vocus PTR-MS. As only the mixing ratio of the sum of the monoterpenes

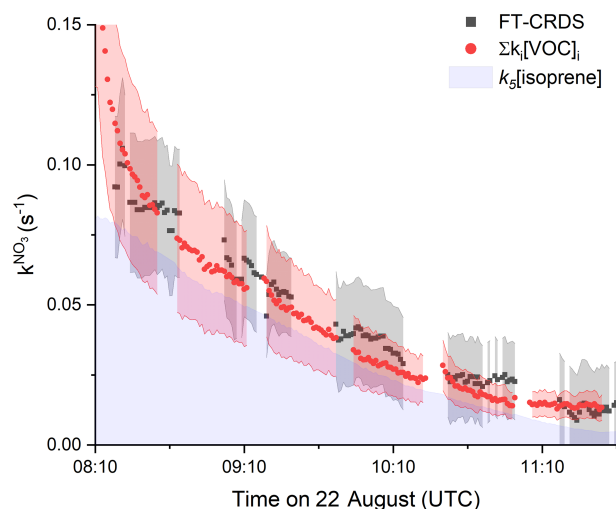


Figure 5. Results from 22 August between 08:00 and 11:40 UTC. Comparison between k^{NO_3} (black data points, uncertainty as grey shaded area) and NO₃ reactivity calculated from $\Sigma k_i[\text{VOC}]_i$ (red data points) using the measured isoprene and Σ monoterpenes mixing ratios. The associated uncertainty (red area) was derived by error propagation by considering the standard deviations of the VOC mixing ratios as well as the uncertainties of the rate coefficients (41 % for k_5 and 47 % for $k_{\text{monoterpenes}}$). The uncertainty of k^{NO_3} was estimated as explained in Fig. 2. The contribution of isoprene to the observed reactivity is indicated by the area in purple.

was known, an average value of the very similar NO₃ rate coefficients (IUPAC, 2020) for limonene, 3-carene and α -pinene was used for the calculation of $\Sigma k_i[\text{VOC}]_i$ with $k_{\text{monoterpenes}} = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (analogously averaged uncertainty of 47 %). Figure 5 indicates very good agreement between measured and calculated NO₃ reactivity, with ~ 70 % of the overall reactivity caused by isoprene, which is indicated by the purple shaded area. Despite being present at much lower mixing ratios than isoprene, the terpenes contribute ~ 30 % to the overall NO₃ reactivity, which reflects the large rate constants for reaction of NO₃ with terpenes.

The experiments described above indicate that, for a chemical system initially containing only isoprene as the reactive organic trace gas, the measured values of k^{NO_3} can be fully assigned to the isoprene present in the chamber over the course of its degradation. During the NO₃ISOP campaign, not only NO₃ reactivity but also OH reactivity (k^{OH}) was measured; the experimental technique is described briefly in the Supplement. A detailed analysis of the OH reactivity data set will be subject of a further publication, and in Fig. S1 we only compare values of k^{NO_3} and k^{OH} obtained directly after isoprene injections, where k^{OH} should not be significantly influenced by the reaction of OH with secondary products. As shown in Fig. S2, isoprene concentrations derived from both k^{NO_3} and k^{OH} are generally in good agreement when [isoprene] < 5 ppbv.

The oxidation of isoprene by NO₃ in air results in the formation of stable (non-radical) products as well as organic peroxy radicals (RO₂) that can also react with NO₃. As radicals (e.g. NO₃, RO₂ and HO₂) are not sampled by the FT-CRDS, the equivalence of k^{NO_3} and $k_5[\text{isoprene}]$ indicates that non-radical, secondary oxidation products do not contribute significantly to the NO₃ reactivity.

3.2 Steady-state and model calculations: role of RO₂ and chamber walls

The contribution of RO₂, HO₂ and stable products to NO₃ reactivity was examined using a box model based on the chemical mechanistic oxidation processes of isoprene by NO₃, OH and O₃ as incorporated in the Master Chemical Mechanism, version 3.3.1 (Saunders et al., 2003; Jenkin et al., 2015; Khan et al., 2015). A numerical simulation (Fig. 6) of the evolution of NO₃ reactivity was initialized using the experimental conditions of the first isoprene injection on 10 August (5.5 ppbv NO₂, 60 ppbv O₃ and 2 ppbv isoprene, dry air), including chamber-specific parameters such as temperature, the NO₃ and N₂O₅ wall loss rates (quantified in detail below), and the dilution rate. In the model, NO₃ reacts with both stable products and peroxy radicals. One of several major stable oxidation products according to MCM is an organic nitrate with aldehyde functionality (O₂NOC₄H₆CHO, NC4CHO). As the corresponding rate coefficient for the reaction of this molecule with NO₃ is not known, MCM uses a generic rate coefficient based on the IUPAC-recommended temperature-dependent expression for acetaldehyde + NO₃ scaled with a factor of 4.25 to take differences in molecular structure into account. The maximum modelled mixing ratio of NC4CHO was ~ 5 ppbv in type 2 experiments, which would result in a NO₃ reactivity of 0.001 s^{-1} . This value is below the instrument's LOD and would only become observable at extremely low isoprene concentrations. As apparent in Fig. 6, the contribution of stable oxidation products (blue) to the NO₃ reactivity is insignificant compared to the primary oxidation of isoprene (red).

Since the rate coefficients for reaction of isoprene-derived peroxy radicals and NO₃ are (unlike NO₃ + HO₂) poorly constrained by experimental data, the MCM uses a generic value of $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is based on the rate coefficient for the reaction between NO₃ and C₂H₅O₂. The modelled overall NO₃ reactivity when reactions with RO₂ and HO₂ are included (black line) is on average 22 % higher than the reactivity associated only with isoprene, with the major contributors to the additional NO₃ reactivity being nitrooxy isopropyl peroxy radicals (O₂NOC₅H₈O₂, NISOPOO) formed in the primary oxidation step. As neither RO₂ nor HO₂ radicals will survive the inlet tubing (and heated glass flask) between the SAPHIR chamber and the FT-CRDS instrument, our measurement of k^{NO_3} does not include their contribution. The measured values of k^{NO_3} (black data points) scatter around the isoprene-induced reactivity

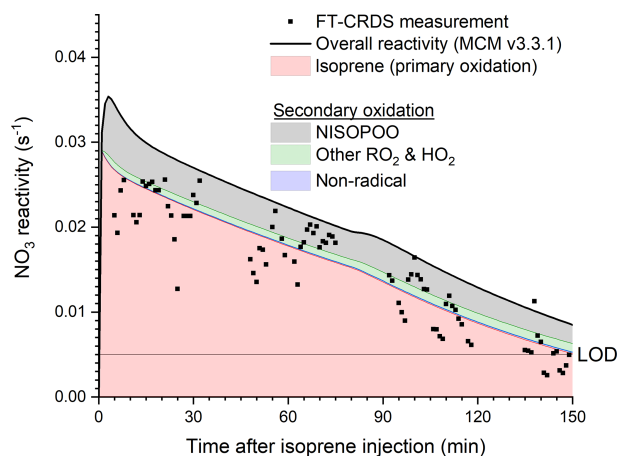


Figure 6. Experimental results for k^{NO_3} and numerical simulation (MCM v3.3.1) of the NO₃ reactivity following the first isoprene injection of the experiment on the 10 August. The simulation was run with 1 min resolution; initial conditions were 60 ppbv of O₃, 5.5 ppbv of NO₂ and 2 ppbv of isoprene and used actual chamber temperatures, which increased from 293 to 301 K during the course of the experiment. Wall losses of NO₃ and N₂O₅ were parameterized as described in the text. Individual contributions to the NO₃ reactivity of isoprene, peroxy radicals and secondary oxidation products are highlighted.

(red), which is understood to result from the minor role of stable (non-radical) oxidation products (blue) in removing NO₃ and the exclusion of peroxy radicals in the measurement.

Another method of deriving NO₃ reactivity is to calculate it from NO₃ (and/or N₂O₅) mixing ratios and production rates under the assumption of steady state as has been carried out on several occasions for the analysis of ambient NO₃ measurements (Heintz et al., 1996; Geyer and Platt, 2002; Brown et al., 2004; Sobanski et al., 2016b). In contrast to our direct measurement of k^{NO_3} , all loss processes (including reaction of NO₃ with RO₂ and HO₂ and uptake of NO₃ and N₂O₅ to surfaces) are assessed using the steady-state calculations. A comparison between k^{NO_3} and NO₃ reactivity based on a steady-state analysis should enable us to extract the contribution of peroxy radicals and wall losses of NO₃ in the SAPHIR chamber. In steady state, the NO₃ reactivity ($k_{\text{ss}}^{\text{NO}_3}$) is derived from the ratio between the NO₃ production rate via Reaction (R2) with rate coefficient k_2 and the mixing ratios of O₃, NO₂ and NO₃ (Eq. 2).

$$k_{\text{ss}}^{\text{NO}_3} = \frac{k_2 [\text{O}_3] [\text{NO}_2]}{[\text{NO}_3]} \quad (2)$$

Acquiring steady state can take several hours if the NO₃ lifetime is long, temperatures are low or NO₂ mixing ratios are high (Brown et al., 2003). In the NO₃ISOP experiments, the NO₃ reactivities were generally high, and steady state is achieved within a few minutes of isoprene being injected into the chamber. However, NO₂ reinjections in the chamber

during periods of low reactivity at the end of an experiment when isoprene was already depleted can lead to a temporary breakdown of the steady-state assumption. In order to circumvent this potential source of error, the non-steady-state reactivities ($k_{\text{nss}}^{\text{NO}_3}$) based on NO₃ and N₂O₅ measurements (McLaren et al., 2010) were calculated using Eq. (3).

$$k_{\text{nss}}^{\text{NO}_3} = \frac{k_2 [\text{O}_3] [\text{NO}_2] - \frac{d[\text{NO}_3]}{dt} - \frac{d[\text{N}_2\text{O}_5]}{dt}}{[\text{NO}_3]} \quad (3)$$

This expression is similar to Eq. (2) except for the subtraction of the derivatives $d[\text{NO}_3]/dt$ and $d[\text{N}_2\text{O}_5]/dt$ from the production term. A comparison of $k_{\text{ss}}^{\text{NO}_3}$ and $k_{\text{nss}}^{\text{NO}_3}$ is given in the Supplement and verifies the assumptions above: as soon as isoprene is injected into the system, $k_{\text{ss}}^{\text{NO}_3}$ and $k_{\text{nss}}^{\text{NO}_3}$ are equivalent (see Fig. S3a), but $k_{\text{ss}}^{\text{NO}_3}$ shows short-term deviations at NO₂ reinjections (see Fig. S3b). As the non-steady-state reactivities are less affected by such events, the latter were used for the comparison with the measured NO₃ reactivities. The steady-state and the non-steady-state calculations are only valid if equilibrium between NO₃ and N₂O₅ is established. Moreover, the N₂O₅ measurements are usually less sensitive to instrument-specific losses under dry conditions. For this reason, measured NO₃ mixing ratios were checked for consistency with the equilibrium to N₂O₅ using the equilibrium constant K_{eq} for Reactions (R3)/(R4) as well as the measured N₂O₅ and NO₂ mixing ratios as denoted in Eq. (4) for this analysis. In the case when a significant deviation was observed, NO₃ mixing ratios from [NO₂], [N₂O₅] and K_{eq} were used.

$$[\text{NO}_3]_{\text{eq}} = \frac{[\text{N}_2\text{O}_5]}{K_{\text{eq}} [\text{NO}_2]} \quad (4)$$

A time series of measured k^{NO_3} and calculated $k_{\text{nss}}^{\text{NO}_3}$ is depicted in Fig. 7a, which shows the results from experiments in the absence of aerosol only. It is evident that $k_{\text{nss}}^{\text{NO}_3}$ is much higher than k^{NO_3} . In Fig. 7b we plot k^{NO_3} versus $k_{\text{nss}}^{\text{NO}_3}$: an unweighted, orthogonal, linear fit has a slope of 0.54 ± 0.01 and indicates that the measured values of k^{NO_3} are almost a factor of 2 lower than $k_{\text{nss}}^{\text{NO}_3}$. Propagation of the uncertainties in k_2 (15 %; IUPAC, 2020) and the NO₃, NO₂ and O₃ mixing ratios (25 %, 9 % and 5 %, respectively) results in an overall uncertainty of 31 % for $k_{\text{nss}}^{\text{NO}_3}$, which cannot account for its deviation to k^{NO_3} .

The fact that $k_{\text{nss}}^{\text{NO}_3}$ is significantly larger than k^{NO_3} indicates that NO₃ can be lost by reactions other than those with reactive, stable VOCs that can be sampled by the FT-CRDS instrument. As discussed above, RO₂ represents the most likely candidate to account for some additional loss of NO₃; the numerical simulations (MCM v3.3.1) predict an additional reactivity of the order of ~ 22 % based on a generic value for $k_{\text{NO}_3+\text{RO}_2}$. However, in order to bring k^{NO_3} and $k_{\text{nss}}^{\text{NO}_3}$ into agreement, either the RO₂ level or the rate coefficient for reaction between NO₃ and RO₂ (especially

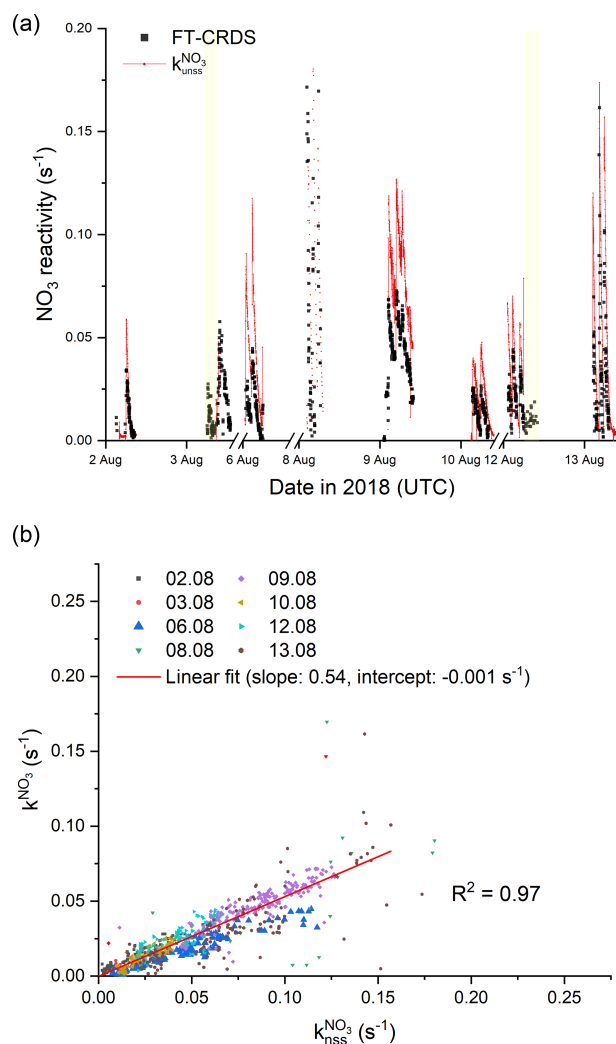


Figure 7. (a) Overview of measured (black) and calculated NO₃ reactivity with Eq. (3) (red). The ticks mark 00:00 UTC of the corresponding day. The yellow areas denote periods with an opened chamber roof. For the sake of clarity, the uncertainties are not included. (b) Correlation plot between $k_{\text{wall}}^{\text{NO}_3}$ and $k_{\text{nss}}^{\text{NO}_3}$. The red line represents an unweighted, orthogonal linear regression ($R^2 = 0.97$) of the complete data set.

NISOPOO) would have to be a factor of 2 larger than incorporated into the model (see below). Alternatively, losses of NO₃ (and N₂O₅) to surfaces enhance $k_{\text{nss}}^{\text{NO}_3}$ but not $k_{\text{wall}}^{\text{NO}_3}$. As no aerosol was present in the experiments analysed above, the only surface available is provided by the chamber walls.

In order to quantify the contribution of NO₃ and N₂O₅ wall losses to $k_{\text{nss}}^{\text{NO}_3}$, we analysed the experiments from the 1 and 2 August during isoprene-free periods, i.e. when no RO₂ radicals are present and (in the absence of photolysis and NO) uptake of NO₃ (or N₂O₅) to the chamber walls represents the only significant sink. Consequently, plotting $k_{\text{nss}}^{\text{NO}_3}$ from this period against $K_{\text{eq}}[\text{NO}_2]$ enables separation of direct NO₃ losses (Reaction R10) from indirect losses via

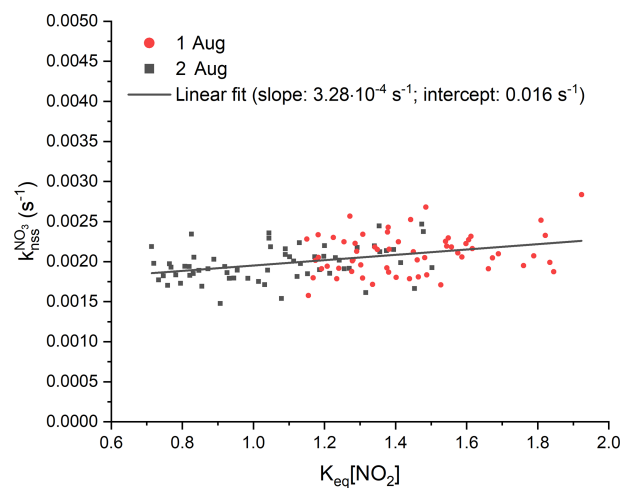


Figure 8. Analysis of the contribution of wall losses of NO₃ and N₂O₅ to NO₃ reactivity, $k_{\text{nss}}^{\text{NO}_3}$, are using experimental data during isoprene-free periods on the 1 August (red) and 2 August (black). Least-squares linear fit of the data is shown with a black line and yielded to an intercept $k_{\text{wall}}^{\text{NO}_3}$ of 0.016 s^{-1} and to a slope $k_{\text{wall}}^{\text{N}_2\text{O}_5}$ of $3.28 \times 10^{-4} \text{ s}^{-1}$. For the sake of better clarity, error bars are not included.

N₂O₅ uptake (Reaction R9) and to derive first-order loss rates ($k_{\text{wall}}^{\text{NO}_3}$ and $k_{\text{wall}}^{\text{N}_2\text{O}_5}$) of NO₃ and N₂O₅ according to Eq. (5) (Allan et al., 2000; Brown et al., 2009b; Crowley et al., 2010; McLaren et al., 2010).

$$k_{\text{nss}}^{\text{NO}_3} = k_{\text{wall}}^{\text{NO}_3} + k_{\text{wall}}^{\text{N}_2\text{O}_5} K_{\text{eq}}[\text{NO}_2] \quad (5)$$

The results from the isoprene-free periods of experiments on the 1 and 2 August are shown in Fig. 8. A linear regression of the data yields a slope ($k_{\text{wall}}^{\text{N}_2\text{O}_5}$) of $(3.28 \pm 1.15) \times 10^{-4} \text{ s}^{-1}$ and an intercept ($k_{\text{wall}}^{\text{NO}_3}$) of $(0.0016 \pm 0.0001) \text{ s}^{-1}$, indicating that NO₃ losses dominate and that heterogeneous removal of N₂O₅ does not contribute significantly to the overall loss rate constant of $\sim 0.002 \text{ s}^{-1}$. The data reproducibility from one experiment to the next indicates that the NO₃/N₂O₅ wall loss rates are unchanged if the experimental conditions, i.e. dry air and no aerosols, are comparable. Humidification of the air, on the other hand, may facilitate heterogeneous reactions of NO₃ or N₂O₅ with the chamber walls and increase corresponding loss rates. This might be an explanation for observation of a larger difference between $k_{\text{wall}}^{\text{NO}_3}$ and $k_{\text{nss}}^{\text{NO}_3}$ during an experiment under humid conditions on the 6 August (Fig. 7b, blue triangles). Lack of extensive isoprene-free periods on this day impede the extraction of wall loss rates with this approach: even after subtraction of $k_{\text{wall}}^{\text{NO}_3}$ from $k_{\text{nss}}^{\text{NO}_3}$, Eq. (5) is not applicable in experiments once isoprene is present (and becomes the dominant sink of NO₃) as reactions of RO₂ indirectly co-determine the NO₂ mixing ratios.

For further analysis, the wall loss rate constants of NO₃ and N₂O₅ were fixed as long as there was neither humidity nor particles in the chamber, and they are considered in-

variant with time after isoprene injections. This implicitly assumes that low-volatility oxidation products that deposit on chamber walls do not enhance the reactivity of the walls to NO₃. As these products have less double bonds than isoprene and react only very slowly with NO₃, this assumption would appear reasonable.

We examined the effect of introducing the NO₃ and N₂O₅ wall loss rate constants calculated as described above into the chemical scheme used in the box model (MCM v3.3.1). The results from three different model outputs for the experiment on the 2 August are summarized in Fig. 9, which compares simulated and measured mixing ratios of NO₃, N₂O₅, NO₂, O₃ and isoprene (following its addition at 11:00 UTC) as well as the measured and non-steady-state NO₃ reactivities k^{NO_3} and $k_{\text{nss}}^{\text{NO}_3}$. The omission of NO₃/N₂O₅ wall losses (model 1) results in simulated NO₃ and N₂O₅ mixing ratios up to 1400 and 1600 pptv, respectively, during the isoprene-free period, which exceed measurements by factors of 4–8. This is because the only loss process for these species in this phase is the dilution rate that is 2 orders of magnitude lower than the estimated wall loss rates. Such high amounts of NO₃/N₂O₅ in the parts per billion range result in rapid depletion of nearly half of the total injected isoprene within the first minute, which is why model 1 cannot describe the measurements either before or after the injection. Model 2 (red lines) includes the estimated wall loss rates and reproduces the measurements more accurately: the NO₂ and O₃ mixing ratios are accurately simulated. Furthermore, NO₃ and N₂O₅ mixing ratios that are only 10 % to 30 % higher than those measured and therefore NO₃ reactivities lower than $k_{\text{nss}}^{\text{NO}_3}$ (orange circles) are predicted.

The evolution of the isoprene mixing ratio is reproduced by the model, which is why k^{NO_3} (mostly determined by $k_5[\text{isoprene}]$, purple area) is only slightly lower than the simulated overall reactivity by model 2. After quantification of NO₃/N₂O₅ wall losses, NO₃+RO₂ reactions remain the only source of additional NO₃ reactivity to explain the difference between k^{NO_3} and $k_{\text{nss}}^{\text{NO}_3}$. As already mentioned above, the model may underestimate the effect of RO₂-induced losses of NO₃ either because the RO₂ mixing ratios are underestimated or because the rate coefficient $k_{\text{RO}_2+\text{NO}_3}$ is larger than assumed.

The result of a simulation (model 3) with $k_{\text{RO}_2+\text{NO}_3}$ set to $4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (twice the generic value in MCM v3.3.1) is displayed as the blue lines in Fig. 9. The O₃, NO₂, N₂O₅ and isoprene mixing ratios are only slightly affected by this change in the reaction constant, whereas its impact on the NO₃ mixing ratios as well as on the reactivity is very significant. The higher rate coefficient for reaction of NO₃ with RO₂ would be sufficient for the observed discrepancy between the overall reactivity $k_{\text{nss}}^{\text{NO}_3}$ and k^{NO_3} within the uncertainties associated with the analysis. Optimum agreement irrespective of uncertainties would be achieved with a value of $9.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{\text{RO}_2+\text{NO}_3}$ (i.e. a factor of 4 higher than in MCM), which is demonstrated in

a comparable experiment under dry conditions on the 10 August (see Fig. S4 in the Supplement).

There are only few experimental studies on reactions of NO₃ with RO₂, and the rate coefficient for reaction of NO₃ with isoprene-derived RO₂ has never been measured. For the reaction between NO₃ and the methyl peroxy radical (CH₃O₂), values between 1.0×10^{-12} and $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ have been reported (Crowley et al., 1990; Biggs et al., 1994; Daele et al., 1995; Helleis et al., 1996; Vaughan et al., 2006), with a preferred value of $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006). Increasing the length of the C–C backbone in the peroxy radical appears to increase the rate coefficient, with values of $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ preferred for reaction of NO₃ with C₂H₅O₂ (Atkinson et al., 2006), whereas the presence of electron-withdrawing groups attached to the peroxy carbon atom reduces the rate coefficient (Vaughan et al., 2006). A single study of the reaction between NO₃ and an acylperoxy radical indicates that the rate coefficient ($4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) may be larger than the MCM adopted value of $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Canosa-Mas et al., 1996). Similarly, an indirect study (Hjorth et al., 1990) of the rate coefficient for the reaction between NO₃ and a nitro-substituted C₆ peroxy radical ((CH₃)₂C(ONO₂)C(CH₃)₂O₂) reports a value of $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which may be appropriate for longer-chain peroxy radicals derived from biogenic trace gases. In light of the large uncertainty associated with the kinetics of RO₂ + NO₃ reactions, a rate coefficient of $4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction between NISOPOO and NO₃ is certainly plausible.

We note, however, that use of a faster rate coefficient for the reaction between RO₂ and NISOPOO, RO₂ isomerization processes and differentiation between the fates of the main NISOPOO isomers as proposed by Schwantes et al. (2015) would result in lower RO₂ mixing ratios. If $k_{\text{NISOPOO}+\text{RO}_2}$ in MCM v3.3.1 is set to a value of $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average over all isomers, Schwantes et al., 2015), a slightly higher value of $5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{\text{RO}_2+\text{NO}_3}$ would be necessary to bring modelled and measured NO₃ reactivity into agreement within associated uncertainties. Conversely, increasing RO₂ concentrations by the required factor of 2 would necessitate a significant reduction in the model rate coefficients for RO₂ + RO₂ or RO₂ + HO₂ reactions, which contradicts experimental results (Boyd et al., 2003; Schwantes et al., 2015) and is considered unlikely.

Differences in measurement of $k_{\text{nss}}^{\text{NO}_3}$ and modelled NO₃ reactivity could also result from incorrectly modelled product yields, owing to the simplified mechanism used, which, for example, does not consider in detail the formation of methyl vinyl ketone (MVK) via β-NISOPOO isomers or the reaction between NO₃ and other main products like hydroxy isopropyl nitrates (e.g. O₂NOCH₂C(CH₃)CHCH₂OH, ISOPCNO₃) and nitrooxy

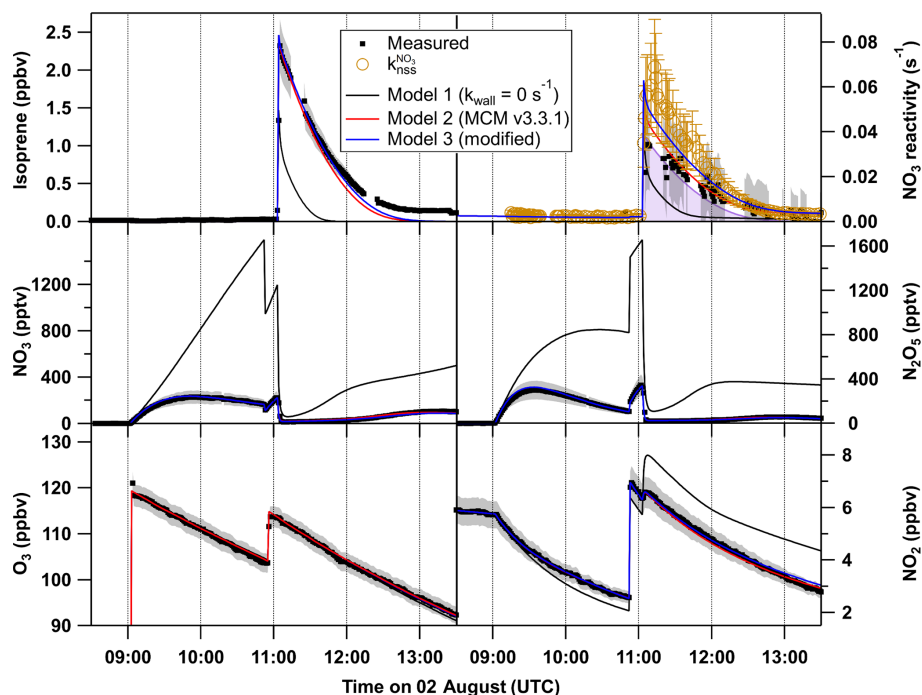


Figure 9. O₃, NO₂, NO₃, N₂O₅ and isoprene mixing ratios and NO₃ reactivity on 2 August (black). The grey shaded area symbolizes the overall uncertainty associated with each measurement. Orange circles denote the reactivity obtained using Eq. (3). The results of the numerical simulation using MCM v3.3.1 with NO₃ and N₂O₅ wall loss rates set to 0 s⁻¹ (model 1) are shown by black lines. The model output with introduction of NO₃ and N₂O₅ wall loss rates of 0.016 s⁻¹ and 3.3 × 10⁻⁴ s⁻¹, respectively, for each of the reactants is shown by a red line (model 2), whereas the blue line (model 3) shows the result of model 2 with the rate coefficient for reaction between NO₃ and RO₂ set to 4.6 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, which is twice the value estimated by the MCM.

isopropyl hydroperoxide (O₂NOCH₂C(CH₃)CHCH₂OOH, NISOPOOH). However, none of these products is expected to react sufficiently rapidly with NO₃ to make a difference: the rate coefficient for reaction of NO₃ with MVK is < 6 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ and that for 2-methyl-3-butene-2-ol (a comparable molecule to ISOPCNO₃) is 1.2 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 298 K (IUPAC, 2020). Even parts per billion amounts of these products would not cause significant additional NO₃ reactivity.

On the other hand, the FT-CRDS will underestimate the reactivity of NO₃ if products that are formed do not make it to the inlet (i.e. traces gases with high affinity for surfaces). One potential candidate for this category is NISOPOOH, formed in the reaction between NISOPOO and HO₂. There are no kinetic data on the reaction of NO₃ with NISOPOOH, though given the lack of reactivity of NO₃ towards organic peroxides it is very unlikely that the rate coefficient would be larger than for NO₃ + O₂NOCH₂C(CH₃)=CHCHO. Analysis of one experiment (9 August, Fig. 7b), in which HO₂ production (and thus the yield of NISOPOOH) was enhanced by the addition of propene and CO, shows that the difference between k^{NO_3} and $k_{\text{nss}}^{\text{NO}_3}$ on that day is comparable to those of the other experiments. This would also indicate that the influence of the potential non-detection of the hydroperoxide on the analysis should be low.

All in all, the results of the analysis above strongly suggest that the difference between directly measured and non-steady-state reactivity $k_{\text{nss}}^{\text{NO}_3}$ is caused by reactions of NO₃ with RO₂ with the results best explained when a rate coefficient of ~ 5 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ is used. Quantifying the impact of peroxy radicals on the fate of NO₃, however, is challenging. The rate coefficients for RO₂ + NO₃ are scarce and uncertain and the rate constants for self-reaction of RO₂ derived from NO₃ + isoprene have not been determined in direct kinetic measurement but via analyses of non-radical product yields.

4 Summary and conclusion

Direct measurements of NO₃ reactivity (k^{NO_3}) in chamber experiments exploring the NO₃-induced oxidation of isoprene showed excellent agreement with NO₃ loss rate constants calculated from isoprene mixing ratios, thus underlining the reliability of the reactivity measurements even under unfavourable conditions with as much as 25 ppbv of NO₂ in the chamber. The main contributor to the overall uncertainty in k^{NO_3} is the correction (via numerical simulation) for the reaction of NO₃ with NO₂ and the thermal decomposition of the N₂O₅ product. The results of the NO₃ISOP campaign

indicate that previously derived overall uncertainties (Liebmann et al., 2017) that considered an uncertainty of 10 % in the rate coefficients of both reactions (Burkholder et al., 2015) and an 8 % uncertainty for the NO₂ mixing ratios are too large.

The measured reactivity, k^{NO_3} , could be completely assigned to the reaction between NO₃ and isoprene, indicating that contributions from reactions of non-radical oxidation products are minor, which is consistent with predictions of the current version of the Master Chemical Mechanism.

Values of NO₃ reactivity as calculated from NO₃ and N₂O₅ mixing ratios and the NO₃ production term were found to be a factor of ~ 1.85 higher than the directly measured NO₃ reactivities (k^{NO_3}). A box model analysis indicates that the most likely explanation is a larger fractional loss of NO₃ via reactions with organic peroxy radicals (RO₂) formed during the oxidation of isoprene. A rate coefficient ($k_{\text{RO}_2+\text{NO}_3} \sim 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is necessary to align model predictions (MCM v.3.3.1) and observations within associated uncertainties.

Data availability. The data from the experiments in the SAPHIR chamber used in this work are available on the EUROCHAMP data home page (<https://data.eurochamp.org/data-access/chamber-experiments/>, EUROCHAMP, 2020).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-20-10459-2020-supplement>.

Author contributions. HF, AN and SSB designed and conducted the chamber experiments. PD, JML and JaS were responsible for the NO₃ reactivity measurements. CC and AN were responsible for the OH reactivity measurements. JuS, JNC, FB, LZ, SSB and WM were responsible for the NO₃ and N₂O₅ measurements and its evaluation. KX, RH, RT and DR were responsible for the PTR-MS measurements of VOCs. PD, NF, JML and JuS took and evaluated NO₂ and NO_x data. FR was responsible for O₃ and NO measurements. PD did the analysis and, with the help of JNC, wrote the paper. JL, HF, SSB, AN, CC, JML, FB, RH, KX and RT contributed to the article.

Competing interests. The authors declare that they have no conflict of interest.

Special issue statement. This article is part of the special issue “Simulation chambers as tools in atmospheric research (AMT/ACP/GMD inter-journal SI)”. It is not associated with a conference.

Acknowledgements. We thank Chemours for provision of the FEP sample used to coat the cavities and flow tube reactor of the NO₃ reactivity setup.

Financial support. This research has been supported by Horizon 2020 (EUROCHAMP-2020 (grant no. 730997) and SARLEP (grant no. 681529)) and French National Research Agency/Labex VOLTAIRE (grant no. ANR-10-LABX-100-01).

The article processing charges for this open-access publication were covered by the Max Planck Society.

Review statement. This paper was edited by Thomas Karl and reviewed by two anonymous referees.

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