

Chamber studies of NO₃ reactivity during the oxidation of isoprene

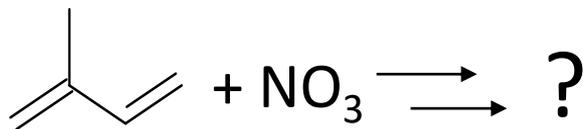


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Utrecht University



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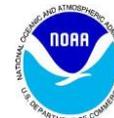
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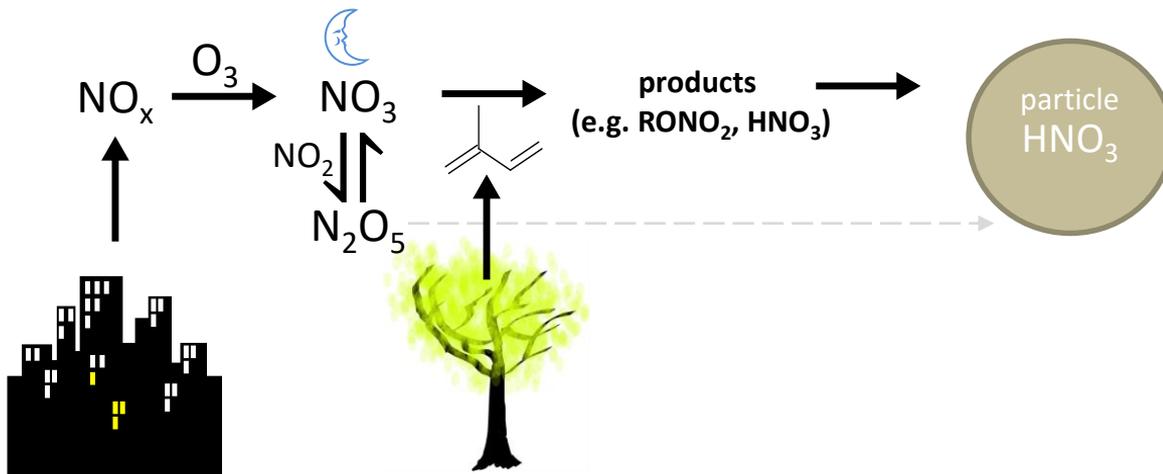


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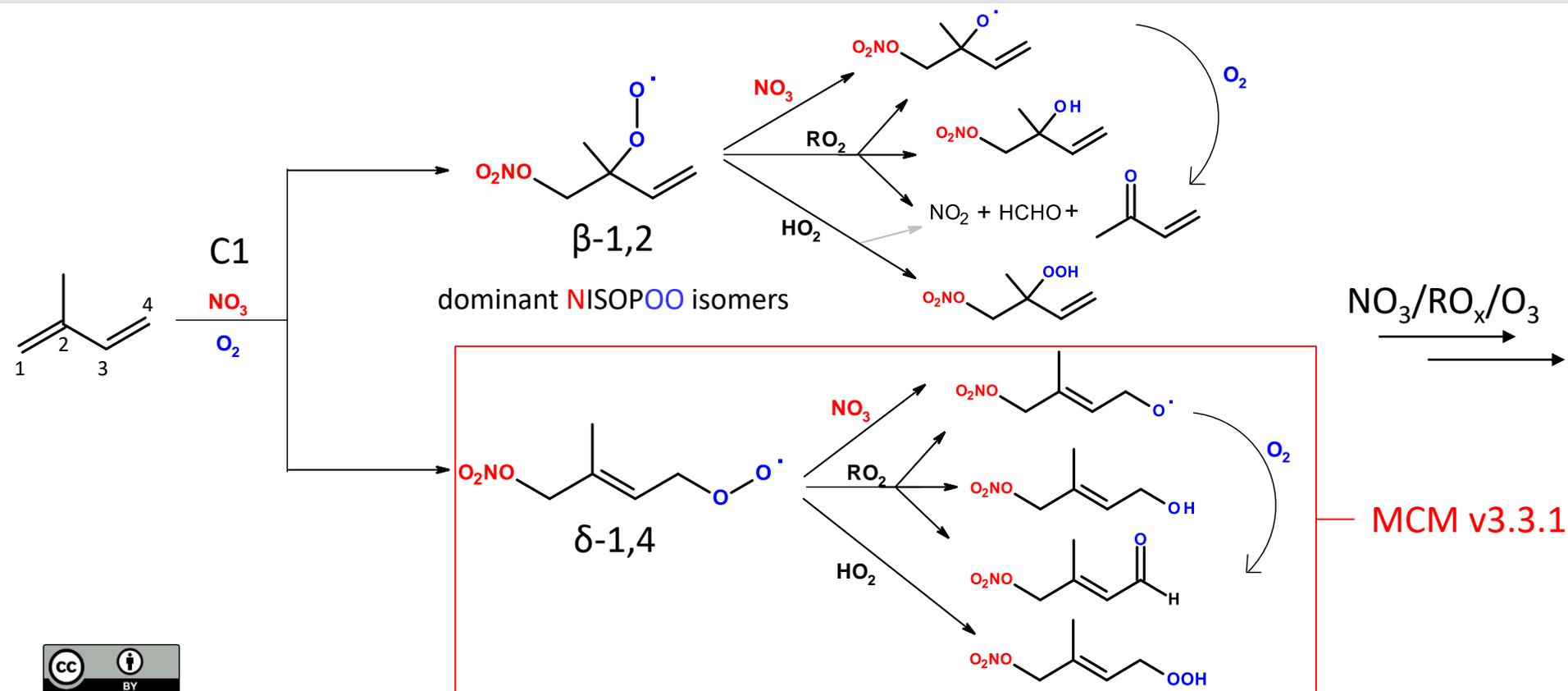


Motivation: Why investigating NO_3 + isoprene?

- Isoprene is the major (non-methane) VOC from biogenic emission sources
- The nitrate radical (NO_3) becomes an important oxidizing agent at night-time
- Products from isoprene oxidation by NO_3 can form secondary organic aerosols (SOA) -> irreversible NO_x removal from gas phase



The NO_3 + isoprene system: Primary & secondary oxidation



What has been done? “NO₃ISOP SAPHIR” campaign

- intensive product study of the NO₃ + isoprene system at the atmospheric simulation chamber SAPHIR of Forschungszentrum Jülich (Germany) in August 2018



Key features of SAPHIR chamber

- > volume: 270 m³, surface: 320 m²
- > FEP double-wall
- > ambient p and T
- > shutter system for exposure to sunlight

- 22 experiments under different conditions (high/low RO₂ or HO₂, dry/humid, daytime/nighttime, aerosol)
 - > NO₃ formation from NO₂/O₃ injections
 - > isoprene injections

Aims of “NO₃ISOP SAPHIR” campaign // Scope of this work

- Better understanding of secondary nighttime and daytime oxidation chemistry
- Testing of chemical mechanisms (especially NO₃ + RO₂, RO₂ + RO₂, RO₂ + HO₂ reaction paths) at different atmospheric conditions
- SOA formation, product study

This work: NO₃ reactivity (k^{NO_3}) during isoprene oxidation

-> Fate of NO₃/N₂O₅

-> Impact of secondary oxidation processes on k^{NO_3}

Direct measurements of
 k^{NO_3}

Comparison with k^{NO_3} derived from:

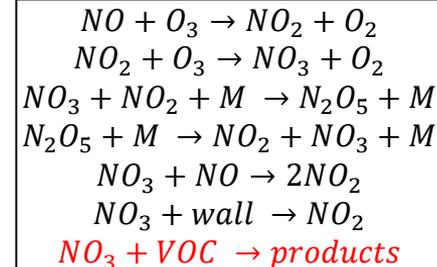
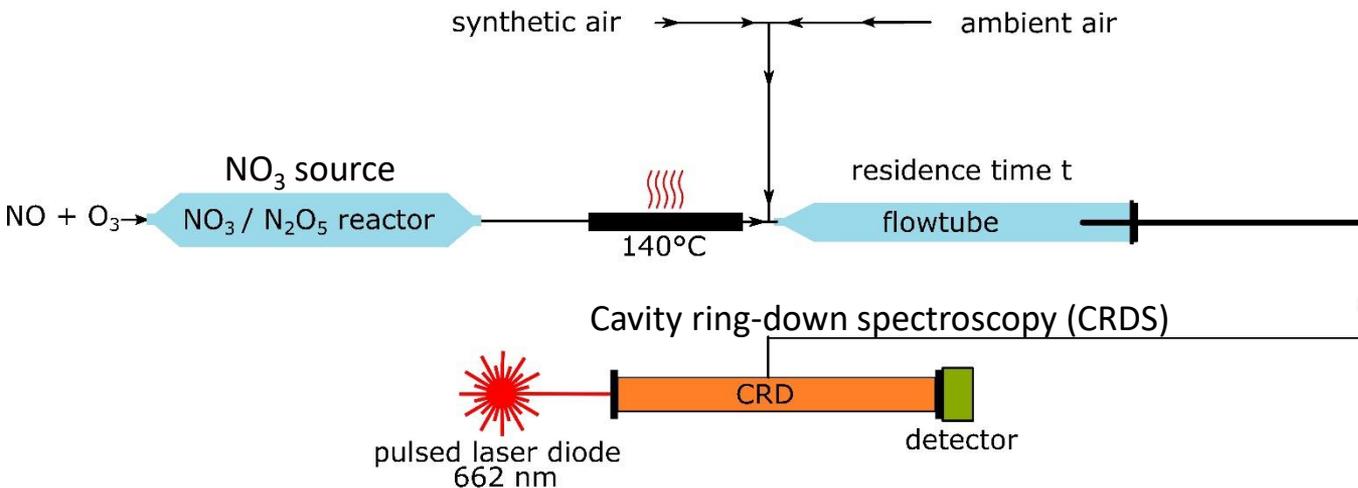
VOC measurements

(un)steady-state

calculations from measured
NO₃, N₂O₅, NO₂ and O₃

model calculations

Direct measurements of k^{NO_3} via CRDS



Performance

LOD: 0.005 s⁻¹

uncertainty dependent on NO_2/k^{NO_3}

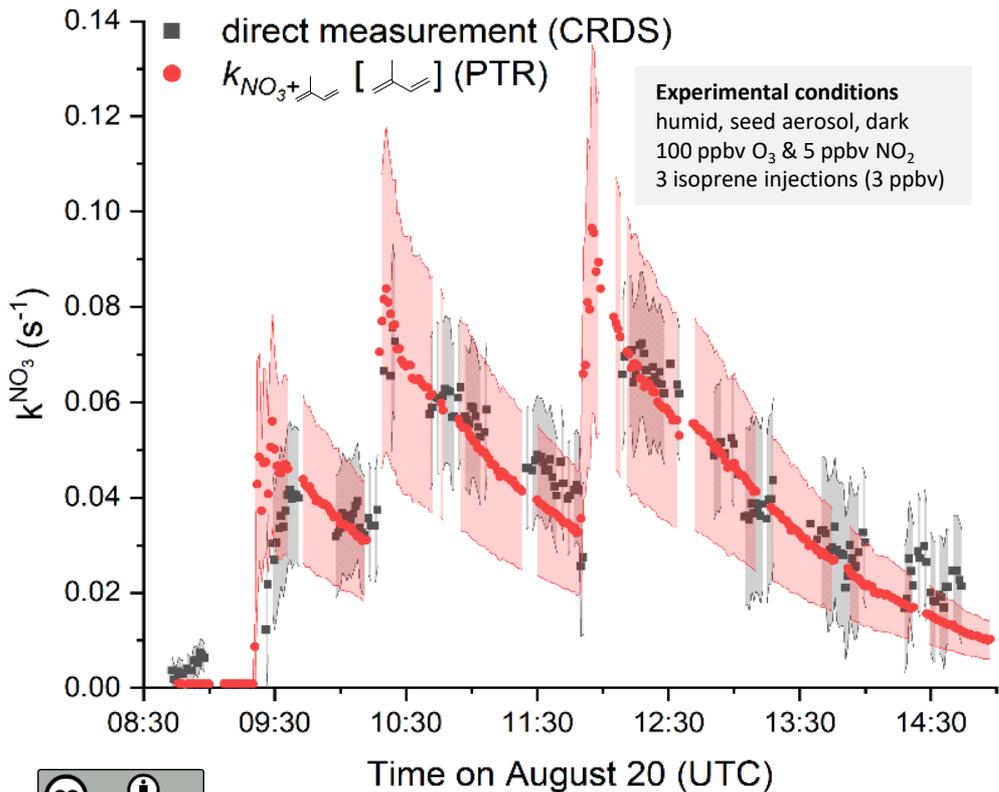
Ambient radicals not sampled

- Ambient or synthetic air (SA) mixed with NO_3 from source
- Remaining NO_3 after reaction in flowtube reactor quantified via CRDS
- Extraction of k^{NO_3} from NO_3 depletion in ambient air compared to SA

-> k^{NO_3} exclusively from VOCs after correction for NO_2 , NO and reactor wall losses



Comparison to VOC measurements – Case study



$$k^{NO_3} = \sum k_i \cdot [VOC]_i$$

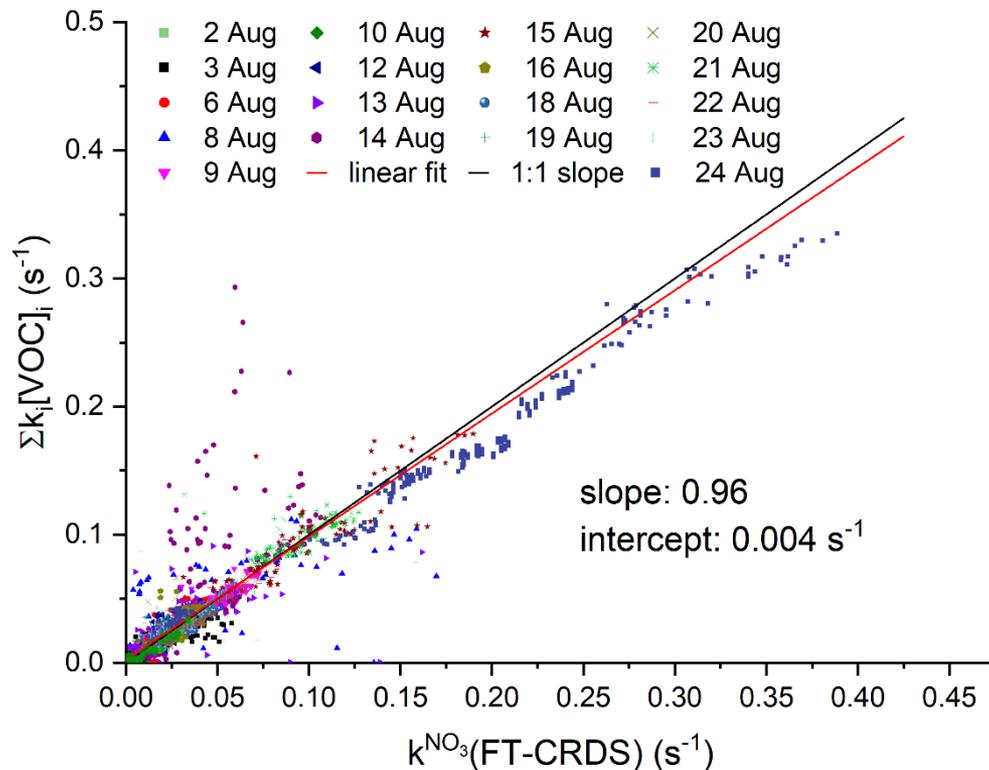
k_i : rate coefficient for
reaction $NO_3 + VOC$

- NO_3 reactivity equal to summed first-order loss rates attributed to all VOCs in chamber (isoprene only for most experiments, i.e. $k^{NO_3} = k_{NO_3+\text{isoprene}} \cdot [\text{isoprene}]$)
- Isoprene mixing ratios available from PTR-ToF-MS measurements

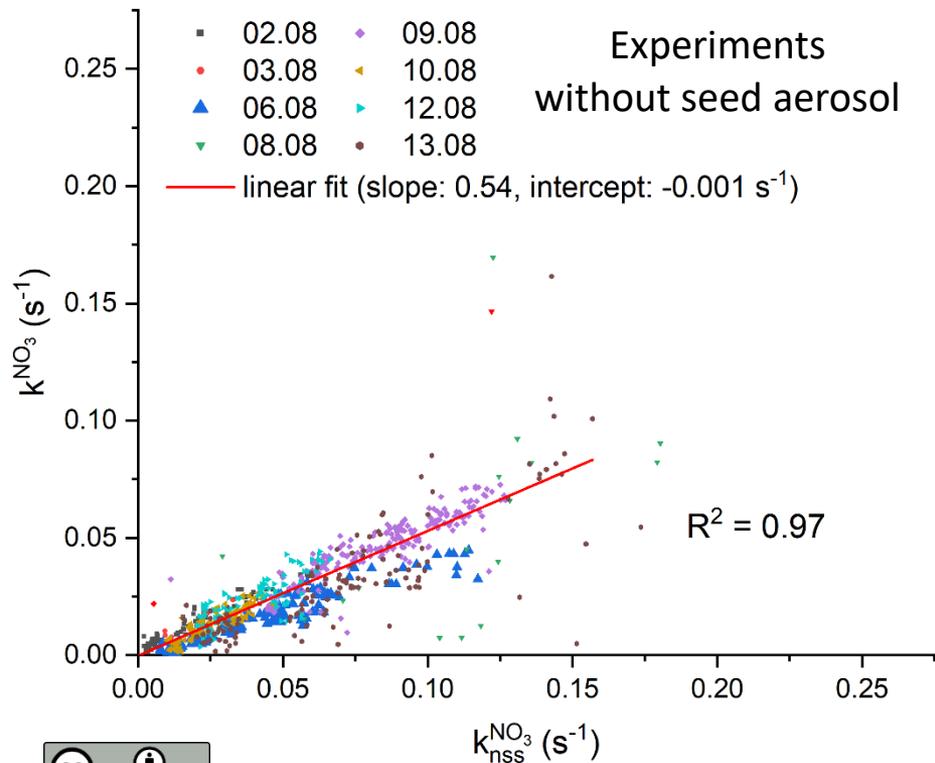
Comparison to VOC measurements - Overview

- Linear regression of correlation plot between k^{NO_3} and $\sum k_i[VOC]_i$ yields slope of 0.96 for whole data set
 - > measured can be fully assigned to primary oxidation step of VOCs

- Measured reactivity can be fully assigned isoprene (and propene or monoterpenes if present) within uncertainties
 - > insignificant contribution of non-radical oxidation products to k^{NO_3}
 - > corresponds to predictions of MCM



Comparison to unstationary-state calculations



$$k_{nss}^{NO_3} = \frac{k_{NO_2+O_3}[O_3][NO_2] - \frac{d[NO_3]}{dt}}{[NO_3]} - \frac{d[N_2O_5]}{dt}$$

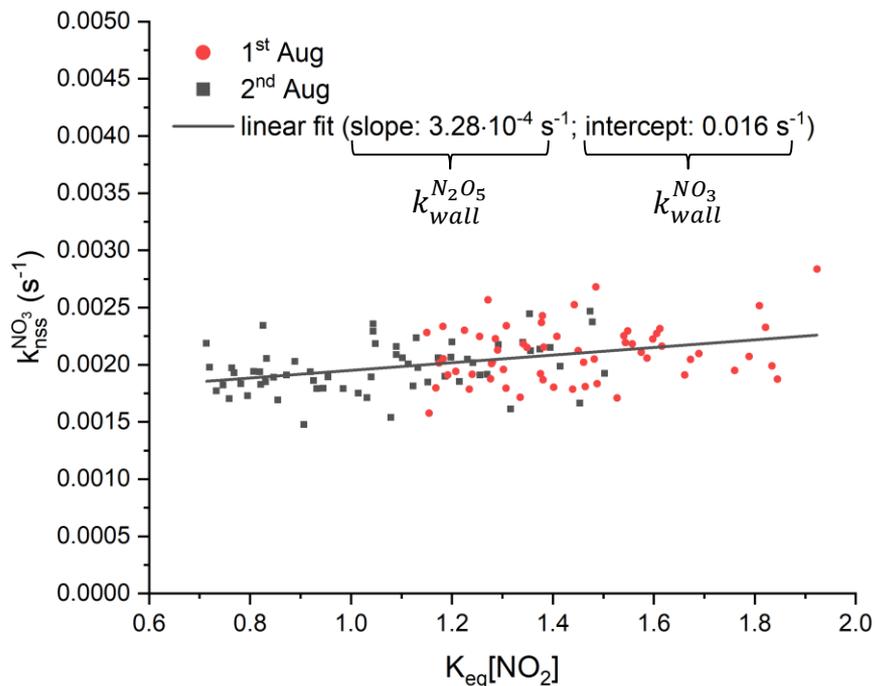
- Unstationary-state calculations from NO₃, O₃, NO₂ and N₂O₅ measurements lead to overall NO₃ reactivity $k_{nss}^{NO_3}$ including every loss path
- $k_{nss}^{NO_3}$ is on average a factor of ~1.85 higher than measured k^{NO_3} during experiments without any seed aerosol

Remaining reasons for discrepancy

- NO₃/N₂O₅ losses on chamber walls
- Species not sampled by CRDS, most likely RO₂ radicals



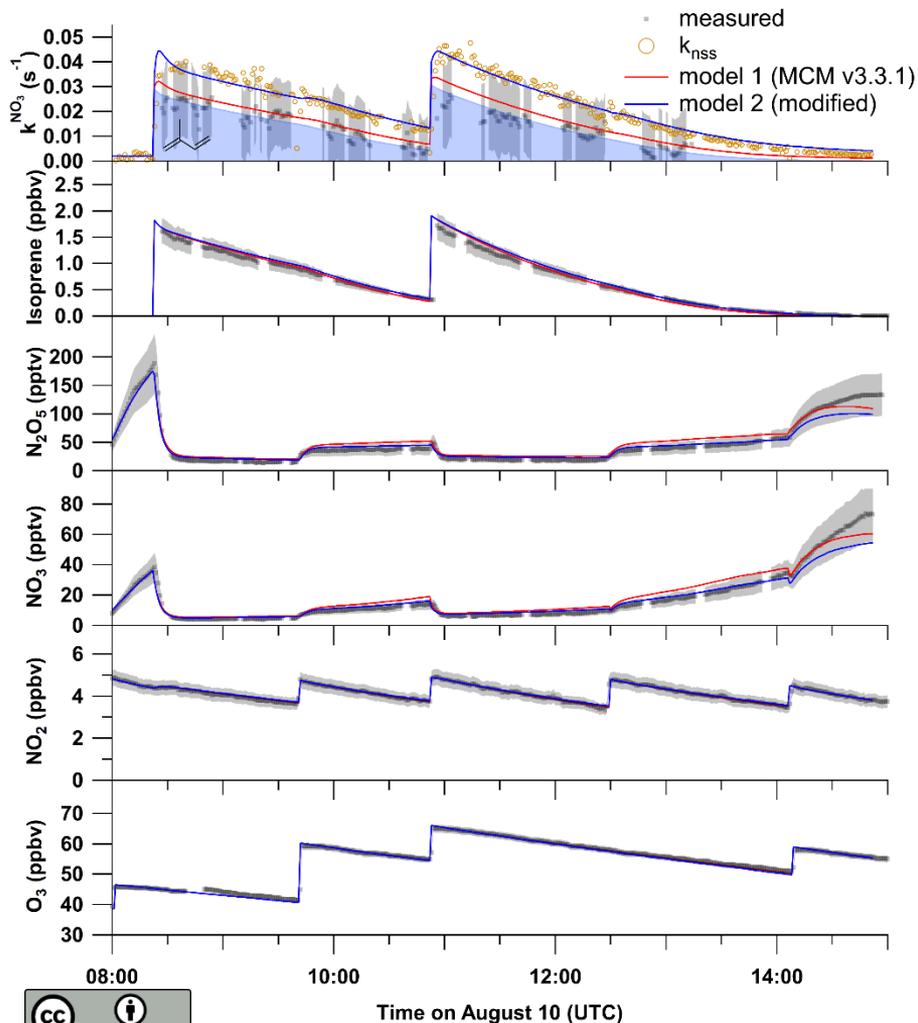
Estimation of $\text{NO}_3/\text{N}_2\text{O}_5$ wall losses in SAPHIR chamber



- During isoprene-free periods chamber walls remain only loss source -> used for quantification

$$\underbrace{k_{nss}^{NO_3}}_y = \underbrace{k_{wall}^{NO_3}}_{\text{intercept}} + \underbrace{k_{wall}^{N_2O_5}}_{\text{slope}} \underbrace{K_{eq}[\text{NO}_2]}_x$$

- Direct and indirect NO_3 wall loss rate too small to explain higher $k_{nss}^{NO_3}$ during isoprene oxidation



Comparison to model calculations (MCM v 3.3.1)

Impact of RO₂ assessed with MCM Case study: Experiment on August 10

Model 1: MCM v3.3.1 with SAPHIR chamber characteristics

Model 2: same as Model 1 but with doubled $k_{NO_3+RO_2}$ of $4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

- Model 1 (MCM) expects additional NO₃ reactivity of only ~22% from secondary oxidation with RO₂ radicals as main contributor
- Agreement would be achieved if generic rate coefficient of NO₃ + RO₂ in MCM would be doubled

Summary

- Directly measured NO_3 reactivities can be fully assigned to primary oxidation of isoprene
 - > Secondary oxidation of non-radical products by NO_3 is insignificant
 - > consistent with current version of MCM
- NO_3 reactivities derived from unstationary-state calculations are a factor of 1.85 higher than measured k^{NO_3}
 - > additional reactivity might be caused by reaction of NO_3 with RO_2 radicals
 - > current version of MCM expects additional reactivity from RO_2 of 22% only
 - > rate coefficient of $\text{NO}_3 + \text{RO}_2$ in MCM has to be doubled to $4.6 \times 10^{-12} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ to bring model results and measurements into agreement