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► **To cite this version:**

Philip T. M. Carlsson, Luc Vereecken, Anna Novelli, François Bernard, Birger Bohn, et al.. The role of radical chemistry in the product formation from nitrate radical initiated gas-phase oxidation of isoprene. vEGU21, 2021, Online, France. 10.5194/egusphere-egu21-7338 . insu-03559374

HAL Id: insu-03559374

<https://hal-insu.archives-ouvertes.fr/insu-03559374>

Submitted on 7 Feb 2022

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EGU21-7338

<https://doi.org/10.5194/egusphere-egu21-7338>

EGU General Assembly 2021

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The role of radical chemistry in the product formation from nitrate radical initiated gas-phase oxidation of isoprene

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Experiments at atmospherically relevant conditions were performed in the simulation chamber SAPHIR, investigating the reaction of isoprene with NO₃ and its subsequent oxidation. Due to the production of NO₃ from the reaction of NO₂ with O₃ as well as the formation of OH in subsequent reactions, the reactions of isoprene with O₃ and OH were estimated to contribute up to 15% of the total isoprene consumption each in these experiments. The ratio of RO₂ to HO₂ concentrations was varied by changing the reactant concentrations, which modifies the product distribution from bimolecular reactions of the nitrated RO₂. The reaction with HO₂ or NO₃ was found to be the main bimolecular loss process for the RO₂ radicals under all conditions examined.

Yields of the first-generation isoprene oxygenated nitrates as well as the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) were determined by high resolution proton mass spectrometry using the Vocus PTR-TOF. The experimental time series of these products are compared to model calculations based on the MCM v3.3.1,¹ the isoprene mechanism as published by Wennberg *et al.*² and the newly developed FZJ-NO₃-isoprene mechanism,³ which incorporates theory-based rate coefficients for a wide range of reactions.

Among other changes, the FZJ-NO₃-isoprene mechanism contains a novel fast oxidation route through the epoxidation of alkoxy radicals, originating from the formation of nitrated peroxy radicals. This inhibits the formation of MVK and MACR from the NO₃-initiated oxidation of isoprene to practically zero, which agrees with the observations from chamber experiments. In addition, the FZJ-NO₃-isoprene mechanism increases the level of agreement for the main first-generation oxygenated nitrates.

¹ M. E. Jenkin, J. C. Young and A. R. Rickard, The MCM v3.3.1 degradation scheme for isoprene, *Atmospheric Chem. Phys.*, 2015, **15**, 11433–11459.

² P. O. Wennberg *et al.*, Gas-Phase Reactions of Isoprene and Its Major Oxidation Products, *Chem. Rev.*, 2018, **118**, 3337–3390.

³ L. Vereecken *et al.*, Theoretical and experimental study of peroxy and alkoxy radicals in the NO₃-initiated oxidation of isoprene, *Phys. Chem. Chem. Phys.*, submitted.