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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 NO<sub>3</sub> and its subsequent oxidation. Due to the production of NO<sub>3</sub> from the reaction of NO<sub>2</sub> with O<sub>3</sub> as well as the formation of OH in subsequent reactions, the reactions of isoprene with O<sub>3</sub> and OH were estimated to contribute up to 15% of the total isoprene consumption each in these experiments. The ratio of RO<sub>2</sub> to HO<sub>2</sub> concentrations was varied by changing the reactant concentrations, which modifies the product distribution from bimolecular reactions of the nitrated RO<sub>2</sub>. The reaction with HO<sub>2</sub> or NO<sub>3</sub> was found to be the main bimolecular loss process for the RO<sub>2</sub> 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,<sup>1</sup> the isoprene mechanism as published by Wennberg *et al.*<sup>2</sup> and the newly developed FZJ-NO<sub>3</sub>-isoprene mechanism,<sup>3</sup> which incorporates theory-based rate coefficients for a wide range of reactions.

Among other changes, the FZJ-NO<sub>3</sub>-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 NO<sub>3</sub>-initiated oxidation of isoprene to practically zero, which agrees with the observations from chamber experiments. In addition, the FZJ-NO<sub>3</sub>-isoprene mechanism increases the level of agreement for the main first-generation oxygenated nitrates.

<sup>1</sup> 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.

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

<sup>3</sup> L. Vereecken *et al.*, Theoretical and experimental study of peroxy and alkoxy radicals in the NO<sub>3</sub>-initiated oxidation of isoprene, *Phys. Chem. Chem. Phys.*, submitted.