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

Philip T. M. Carlsson[1], Luc Vereecken[1], Anna Novelli[1], François Bernard[2,6], Birger Bohn[1], Steven S. Brown[3,5], Changmin Cho[1], John Crowley[4], Andreas Hofzumahaus[1], Abdelwahid Mellouki[2], David Reimer[1], Franz Rohrer[1], Justin Shenolikar[4], Ralf Tillmann[1], Li Zhou[2,7], Astrid Kiendler-Scharr[1], Andreas Wahner[1], and Hendrik Fuchs[1]

[1]Institute for Energy and Climate Research, Forschungszentrum Jülich GmbH, Jülich, Germany
[2]Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS (UPR 3021)/OSUC, Orléans, France
[3]NOAA Chemical Sciences Laboratory, Boulder, USA
[4]Atmospheric Chemistry Department, Max-Planck-Institut für Chemie, Mainz, Germany
[5]Department of Chemistry, University of Colorado Boulder, Boulder, USA
[6]now at: Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), Université d'Orléans, Orléans, France
[7]now at: College of Architecture and Environment, Sichuan University, Chengdu, China.

Experiments at atmospherically relevant conditions were performed in the simulation chamber SAPHIR, investigating the reaction of isoprene with NO_3 and its subsequent oxidation. Due to the production of NO_3 from the reaction of NO_2 with O_3 as well as the formation of OH in subsequent reactions, the reactions of isoprene with O_3 and OH were estimated to contribute up to 15% of the total isoprene consumption each in these experiments. The ratio of RO_2 to HO_2 concentrations was varied by changing the reactant concentrations, which modifies the product distribution from bimolecular reactions of the nitrated RO_2. The reaction with HO_2 or NO_3 was found to be the main bimolecular loss process for the RO_2 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-NO_3-isoprene mechanism,[3] which incorporates theory-based rate coefficients for a wide range of reactions.

Among other changes, the FZJ-NO_3-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_3-initiated oxidation of isoprene to practically zero, which agrees with the observations from chamber experiments. In addition, the FZJ-NO_3-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 *at 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.