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Chemistry of peroxy radicals in the atmosphere: experimental study on the role of their reaction with OH radicals

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Peroxy radicals, RO_2, are key species in the atmosphere. They are formed from the reaction of OH radicals with hydrocarbon: $RH + OH + O_2 \rightarrow RO_2 + H_2O$. In polluted environments, RO_2 radicals react predominantly with NO, leading to formation of NO_2 and eventually through photolysis of NO_2 to formation of O_3. At low NO_x concentrations such as in the marine boundary layer or the background troposphere, the lifetime of RO_2 radicals increases and other reaction pathways become competitive. Atmospheric chemistry models have considered until recently only the self- and cross reaction with other RO_2 radicals or with HO_2 radicals as the major fate for RO_2 radicals under low NO_x conditions. Recently, the rate constants for the reaction of peroxy radicals with OH radicals: $RO_2 + OH \rightarrow$ products has been measured for CH_3O_2 and for larger peroxy up to C_4. The reaction is fast and it was shown to become competitive to other sinks. In order to evaluate the impact of this so far neglected sink for peroxy radicals on the composition of remote atmospheres, the reaction products must be known. HO_2 has been identified as major product for the reaction of CH_3O_2 radicals. A recently improved experimental set-up combining laser photolysis with two simultaneous CW-CRDS (continuous wave cavity-ring down spectroscopy) detections in the near IR allowing for a time resolved, absolute quantification of OH and RO_2 radicals has been used for a further investigation of this class of reactions. High-repetition rate LIF is used for determining relative OH profiles. Currently we are investigating the product yields of larger peroxy radicals, and recent results will be presented at the conference.

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