

SEMINAR

Evolution of OH reactivity in low-NO volatile organic compound oxidation investigated by the fully explicit GECKO-A model

Zhe Peng

University of Colorado - Boulder

OH reactivity (OHR) governs the oxidative capacity in the atmosphere but remains poorly constrained. The evolution of OHR during oxidation of volatile organic compounds (VOCs) is an important uncertainty. We use the fully explicit Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) model to study the OHR evolution in the low-NO photooxidation of several VOCs, including decane (an alkane), m-xylene (an aromatic), and isoprene (an alkene). For most precursors, oxidation progressively produces more saturated and functionalized species. Total OHR (including precursor and products, OHR_{VOC}) first increases for decane (as functionalization increases OH rate coefficients), and m-xylene (as much more reactive oxygenated alkenes are formed). For isoprene, C=C bond consumption leads to a rapid drop in OHR_{VOC} before significant production of the first main saturated multifunctional product, i.e., isoprene epoxydiol. The saturated multifunctional species in the oxidation of different precursors have similar average OHR_{VOC} per C atom. The latter oxidation follows a similar course for different precursors, involving fragmentation of multifunctional species to eventual oxidation of C1 and C2 fragments to CO_2 , leading to a similar evolution of OHR_{VOC} per C atom. The total OH consumption during complete oxidation to CO_2 is roughly 3 per C atoms. We also explore the trends in radical recycling ratios. We show that differences in the evolution of OHR_{VOC} in the atmosphere, an environmental chamber, and an oxidation flow reactor (OFR) are generally smaller than between precursors. The Teflon wall losses of oxygenated VOCs in chambers result in substantial deviations of OHR_{VOC} from atmospheric conditions, especially for the oxidation of large precursors, where multifunctional species may suffer near-complete wall losses. Wall-loss corrections with the aid of chemically-explicit models are likely to be necessary in many chamber experiments for OHR_{VOC} research for precursors of the size used here or larger. For OFR, the deviations of OHR_{VOC} evolution from the atmospheric case are mainly caused by low HO_2 -to-OH ratio that delays the conversion of rapidly produced RO_2 to stable products, and by lack of efficient organic photolysis. The former can be avoided by lowering the UV lamp setting in OFR, while the latter is shown to be very difficult to avoid.

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Phone: [\(US\) +1 470-285-0305](tel:+14702850305) PIN: 185 723 460#