

Kinetics of Elementary Steps in the Br-Initiated Oxidation of Alkenes Under Atmospheric Conditions

Patrick L. Laine,^{1,2} Dow T. Huskey,^{3,4} Yoon S. Sohn,⁵
J. Michael Nicovich,³ Michael L. McKee,⁶ and Paul H. Wine^{1,3,*}

¹ School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA

² Now at Department of Earth & Atmospheric Sciences, University of Houston, Houston, TX, USA

³ School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA

⁴ Now at MWH Americas Inc., Atlanta, GA USA

⁵ School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA

⁶ Department of Chemistry & Biochemistry, Auburn University, AL, USA

* Corresponding author: pw7@prism.gatech.edu

The Br-initiated oxidation of alkenes may play a significant role in the chemistry of marine tropospheric environments, particularly in polar regions during ozone depletion events. The bromoalkyl radicals formed via Br + alkene addition reactions typically have relatively weak C–Br bonds such that radical unimolecular decomposition often occurs in competition with radical + O₂ reaction under tropospheric conditions. As a result, the tropospheric rates of Br-initiated oxidations of alkenes can display complex temperature and pressure dependences. Using laser flash photolysis studies of Br kinetics in conjunction with supporting electronic structure calculations, we have investigated (for the first time in most cases) the kinetics and thermochemistry of early elementary steps in the Br-initiated oxidations of several alkenes including ethylene, tetramethyl ethylene (TME),¹ methyl vinyl ketone (MVK), 1,3-butadiene, and isoprene. Elementary steps investigated include hydrogen abstraction, formation/dissociation of bromoalkyl radicals, and formation/dissociation of bromoalkylperoxy radicals. At T < 320 K, hydrogen abstraction occurs at a significant rate only for the Br + TME reaction. Observed rate coefficients for Br addition to all alkenes investigated are large, approaching the gas kinetic limit for Br + TME, Br + 1,3-butadiene, and Br + isoprene (at P = 1 atm). C–Br bond dissociation enthalpies (298 K), extracted from temperature-dependent studies of bromoalkyl radical formation/dissociation kinetics, range from ~30 kJ mol⁻¹ for CH₂CH₂Br to ~70 kJ mol⁻¹ for the most stable radical formed via Br addition to isoprene. Allyl resonance stabilization results in formation of particularly strongly bound bromoalkyl radicals upon addition of Br to the conjugated dienes (1,3-butadiene and isoprene). At 298 K, essentially 100% of the bromoalkyl radicals formed from Br reactions with conjugated dienes react with O₂ in competition with unimolecular decomposition. However, loss of allyl resonance stabilization upon addition of O₂ to the bromoalkyl radicals results in particularly weak C–O bonds in the peroxy radicals formed following Br addition to the conjugated dienes; at higher tropospheric temperatures as well as in competitive kinetics experiments carried out in environmental chambers at temperatures near 298 K, these peroxy radicals are likely to decompose back to bromoalkyl radical + O₂ before undergoing bimolecular reaction.

References

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