Atmospheric Chemistry of Methyl-Perfluoro-Heptene-Ethers (MPHEs): OH Radical Reaction Rate Coefficients, Atmospheric Lifetimes and Global Warming Potentials

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Methyl-Perfluoro-Heptene-Ether ($C_7F_{13}OCH_3$, MPHE) mixtures are currently in use internationally and are being considered for use in the U.S. as a potential replacement for perfluorinated alkane and perfluorinated polyether mixtures (persistent greenhouse gases with atmospheric lifetimes >1000 yrs.) used as heat transfer fluids. The MPHEs have increased reactivity toward the hydroxyl radical (OH) compared to the perfluorinated compounds presently in use. Increased OH reactivity leads to reduced atmospheric lifetimes and global warming potentials (GWPs). It is desirable to know accurate rate coefficients for the reaction of MPHE isomers with OH radicals in order to better understand the atmospheric loss facet of the MPHE life cycle.

Here laboratory studies determined the rate coefficients for the gas-phase reaction of OH with six MPHE isomers (see figure below) at 296 K using a relative rate method. A large range of OH rate coefficient (k) values was observed for the MPHE isomers, which is attributed to structural differences between isomers. k values were also determined for the dueterated analogs (D_3-MPHE) of the six MPHE isomers at 296 K in order to elucidate the contribution of hydrogen abstraction from the $-OCH_3$ moiety to the net rate coefficient. Infrared spectra of a MPHE isomeric mixture were measured as part of this work in order to determine the net MPHE mixture radiative efficiency. The atmospheric implications for MPHE use are discussed in light of the atmospheric lifetimes and GWPs calculated for each isomer. Our results highlight the importance of quantifying k values for all mixture components when determining the atmospheric behavior of isomeric mixtures.

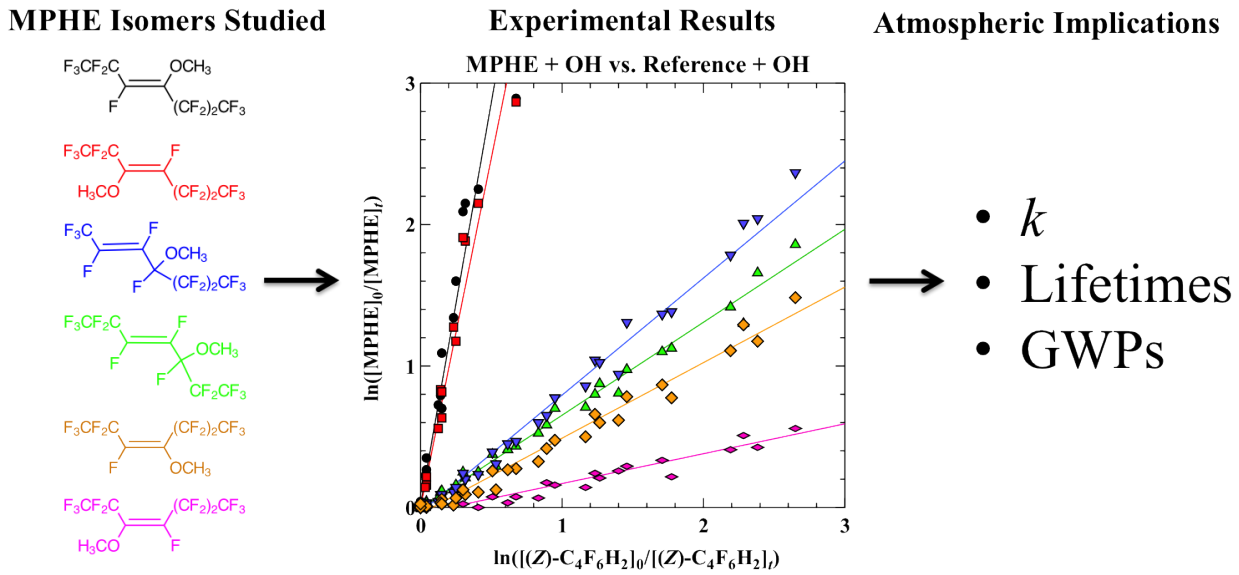

Figure 1. From left to right: MPHE isomers studied, a relative rate plot of MPHE loss due to reaction with OH radicals vs. loss of a reference compound to reaction with OH radicals, and the atmospheric implications of MPHE use. Color of MPHE isomer corresponds to the color of the trace in the relative rate plot.