

Atmospheric Chemistry of Replacement Compounds: OH Reactivity of the (*E*)- and (*Z*)- CF₃CH=CHCF₃

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Unsaturated hydrofluorocarbons (hydrofluoroolefins, HFO) are currently being considered as potential replacements for hydrochlorofluorocarbons and saturated-hydrofluorocarbons in various commercial applications. (*E*)- and (*Z*)- CF₃CH=CHCF₃ are replacement candidates, but before used commercially their atmospheric fate and potential impacts on the environment need to be fully assessed. A significant atmospheric loss process for these compounds is expected to be their gas-phase reaction with the Hydroxyl Radical (OH).

In this work, rate coefficients, *k*, for the reaction of the OH radical with (*E*)- and (*Z*)- CF₃CH=CHCF₃ were measured using two complementary experimental techniques (for this molecule (*E*) is equivalent to *trans*- and (*Z*) is equivalent to the *cis*- isomer). Rate coefficients were measured over a range of temperature (212 – 373) K and total pressure (20 – 600 Torr; He, N₂). The temperature dependences of the rate coefficients were, therefore, determined in the temperature regime most relevant to atmospheric chemistry. The rate coefficients were found to be independent of pressure. The (*E*)- and (*Z*)- isomer reactions have significantly different reactivity and temperature dependent behavior over the temperature range of our study as shown in Figure 1. The differences and possible explanations will be discussed. The atmospheric lifetimes of the (*E*)- and (*Z*)- isomers with respect to loss by reaction with the OH radical are estimated to be ~89 and ~20 days, respectively. As part of this work, infrared absorption spectra of (*E*)- and (*Z*)- isomers were measured and combined with the estimated OH reaction lifetimes to estimate the global warming potentials of 32 and 9.4, respectively, for the 100-year time horizon.

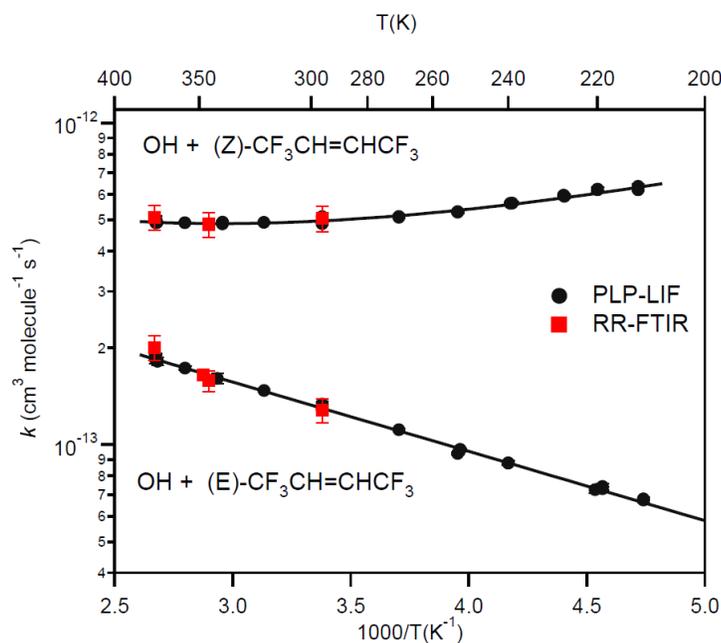


Figure 1. The temperature dependence of the rate coefficients measured for the OH reaction with (*E*)- and (*Z*)- CF₃CH=CHCF₃. PLP-LIF: Pulsed Laser Photolysis – Laser Induced Fluorescence; RR-FTIR: Relative Rate technique combined with Fourier transform infrared detection.