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Atmospheric impact of hydrofluoroethers (HFEs) at a global scale: Can HFEs contribute to the global warming?

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Global concern about the high environmental impact of hydrofluorocarbons (HFCs) led the Kyoto Protocol to list these compounds as potent greenhouse gases. For that reason, hydrofluoroethers (HFEs) were proposed for substitution of HFCs in several applications, such as refrigerants, because of their relatively low global warming potential (GWP). Therefore, it is important to evaluate the impact of future HFE emissions on climate change prior to their widespread use. For that purpose, the most crucial physicochemical parameters to be determined are the rate coefficient for the gas-phase reaction with OH radicals ($k_{OH}(T)$), the main atmospheric diurnal oxidant, and the infrared (IR) absorption cross sections in the atmospheric window (1250-720 cm^{-1}), σ_ν.

In the present work, we present the first experimental determination of $k_{OH}(T)$ between 263 and 353 K for $CF_3CHFCF_2OCH_3$ (HFE-356mec3) and $CHF_2CHFOCF_3$ (HFE-236ea1). The pulsed laser photolysis/laser induced fluorescence technique was employed to generate OH radicals and to monitor their temporal profile.[1] A positive T-dependence of $k_{OH}(T)$ was observed in both reactions and it is well-described by following Arrhenius expressions:

HFE-356mec3: $k_{OH}(T)$ = (1.18±1.07)×10^{-12} exp[-(1046±27)/T] cm^3 $molecule^{-1}$ s^{-1}

HFE-236ea1: $k_{OH}(T)$ = (7.76±4.26)×10^{-13} exp[-(1417±28)/T] cm^3 $molecule^{-1}$ s^{-1}

According to the observed T-dependence of $k_{OH}(T)$, the OH-reactivity towards these HFEs decreases throughout the troposphere since T decreases with altitude. Based on the obtained kinetic results, the atmospheric lifetime of HFE-356mec3 and HFE-236ea1 due to OH-reaction (π_{OH}) was estimated to be 1.2 and 5.5 years, respectively, at sea level (T is considered 298 K). In addition, to evaluate the impact of the emission of 1 kg of the investigated HFEs, σ_ν were determined between 4000-500 cm^{-1}, allowing the calculation of the radiative efficiencies (REs) corrected with π_{OH} [2] and the GWP relative to CO_2 at a time horizon of 100 years. REs were 0.26 and 0.39 W m^{-2} $ppbv^{-1}$ and the resulting GWP at a time horizon of 100 years were 118 and 885 for HFE-356mec3 and HFE-236ea1, respectively. In conclusion, the contribution of HFE-356mec3 and HFE-236ea1 to global warming of Earth could still be significant if their emissions to the atmosphere increase. Despite this fact, HFCs with similar structures ($CH_3CF_2CH_2CF_3$, CHF_2CHFCF_3, or $CH_2FCF_2CF_3$), contribute to the global warming of Earth in much larger extent than the investigated HFEs, presenting GWP between 804 and 8060 [2].

References

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Authors: ESPINOSA GÓMEZ, Sara (UNIVERSIDAD DE CASTILLA-LA MANCHA); JIMÉNEZ MARTÍNEZ, Elena (UNIVERSIDAD DE CASTILLA-LA MANCHA); ALBALADEJO PÉREZ, José (UNIVERSIDAD DE CASTILLA-LA MANCHA)

Presenter: JIMÉNEZ MARTÍNEZ, Elena (UNIVERSIDAD DE CASTILLA-LA MANCHA)

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