



**E2KW
2014**

**Energy and Environment
Knowledge Week**

Toledo, Spain
30th - 31st - OCTOBER



ATMOSPHERIC DEGRADATION OF POTENTIAL CFC REPLACEMENT, HFO-1447fz ($\text{CF}_3(\text{CF}_2)_2\text{CH}=\text{CH}_2$), INITIATED BY OH RADICALS: KINETICS AND SUB-MICRON PARTICLE FORMATION

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ATMOSPHERIC IMPACT OF HFO-1447fz ($\text{CF}_3(\text{CF}_2)_2\text{CH}=\text{CH}_2$): KINETICS AND SUB-MICRON PARTICLE FORMATION INITIATED BY OH RADICALS

1. Purpose

HFC-1447fz ($\text{CF}_3(\text{CF}_2)_2\text{CH}=\text{CH}_2$) is currently being considered as a CFC replacement of HCFC-141b as expansion agent in polyurethane foams. The CFC to be replaced is a potent greenhouse gas (GHG) with a global warming potential (GWP) of 782 relative to CO_2 . To assess the environmental impact of the potential widespread use of HFC-1447fz, an evaluation of the atmospheric degradation initiated by the main atmospheric oxidant (OH radicals) is needed. The rate coefficient (k_{OH}) for the OH + HFC-1447fz reaction (R1) is not known at present. Therefore we present in this work the first gas-phase kinetic study of the OH + HFC-1447fz reaction at room temperature, which allows the estimation of the atmospheric lifetime (τ) of this HFC and its GWP. The obtained k_{OH} allows the estimation of the photochemical ozone creation potential of HFC-1447fz and its impact on regional/local air quality. In addition to the kinetic measurements, the first measurement of the number size distribution of secondary organic aerosols (SOAs) formed in R1 has been also carried out, studying the influence of relative humidity and/or NO_x concentrations in the aerosol formation yield. Particles with particle diameter between 10 and 50 nm are efficiently deposited to alveolar region of lungs. Therefore, these measurements are necessary to understand the effects of aerosol particles on climate and health.

2. Design, Methodology or Approach

Two experimental setups were employed in this study. The first one is based on the pulsed laser photolysis/ laser induced fluorescence (PLP-LIF) technique and was used for performing the kinetic measurements. The second one consists in an atmospheric simulation chamber (ICARE) and was used for detecting the gas-phase and aerosols formed in R1 at room temperature and atmospheric pressure.

2.1. PLP-LIF System at Ciudad Real (Spain): Reaction with OH radicals

The reaction cell consists in a jacketed Pyrex reactor with 200 cm^3 c.a. of internal volume. The temperature was controlled by a thermostatic bath (JULABO, model FP50) and monitored using a chromel-alumel thermocouple. The pressure inside the cell was measured by a capacitance pressure sensor (CERAVAC CTR90 100 Torr and CERAVAC CTR90 1000 Torr). Gas phase of reactants were introduced by calibrated mass flow controllers (Qualiflow AFC 50.00 0-10 sccm, Sierra Instrument INC., C100L 0-14 sccm and Sierra Instrument INC., C100L 0-500 sccm). OH radicals were generated by PLP of precursor (H_2O_2 or HNO_3) at 248 nm using a KrF exciplex laser (Optex, Lambda Physik). They were detected by LIF at 308 nm using a doubled-frequency dye laser (Continuum, ND60) pumped by a Nd:YAG laser (Continuum, NY 81 CS-10).



2.2. ICARE Smog Chamber at Orléans (France): Formation of SOAs

Experiments were carried out in a 7300-L Teflon atmospheric simulation chamber. The chamber is equipped with UV-Vis lamps with maximum emissions centered at 254 nm and 365 nm respectively. Liquid-phase reactants were introduced in an impinger and driven into the chamber by a flow of dry purified air. The chamber is also equipped with different types of analytical instrumentation which are continuously measuring. The temperature and relative humidity were monitored by a combined sensor (T870-Series T800, Dostmann Electronic). Levels of O₃, NO and NO₂ were measured using ozone (Horiba APOA-360) and NO_x (Horiba APNA-360) monitors. Measurements of size distribution of SOA were performed by a scanning mobility particle sizer (SMPS, model TSI 3080) combined with a condensation particle counter (CPC, model TSI 3022A). The SMPS contains a differential mobility analyzer (DMA, model TSI 3081) that allows to separate sub-micron particles with sizes between 10 and 500 nm.

3. Results

The rate coefficients k_{OH} at 298 ± 2 K were observed to be independent on total pressure between 50 and 650 Torr. The average value of k_{OH} is reported to be $(1.09 \pm 0.24) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Assuming an average OH concentration of 10⁶ cm⁻³ in the atmosphere, the lifetime is estimated to be 11 days. GWP corrected with lifetime was estimated to be negligible 0.32 at a horizon time of 100 years compared to that of the main GHG, CO₂. Moreover, the estimated photochemical ozone creation potential (ϵ_{POCP}) relative to ethylene (POCP = 100) was calculated to be 4.9. Regarding the formation of sub-micron particles, it was observed that the number size distribution of these SOAs formed in the reaction of OH radicals with HFC-1447fz is extended to particle diameters between 100 and 130 nm. The yield of SOAs in the absence of NO_x is (1.92 ± 0.06) %, while it is (0.064 ± 0.003) % in the presence of 1.34 ppm of NO_x.

4. Conclusions

- HFC-1447fz (CF₃(CF₂)₂CH=CH₂) reacts quite fast with OH radicals. As a consequence it can be degraded in around 11 days, avoiding its accumulation in the troposphere and minimizing the direct effect on the global warming of Earth.
- Degradation of HFC-1447fz (CF₃(CF₂)₂CH=CH₂) will yield negligible amounts of ground ozone, according to the ϵ_{POCP} calculation.
- Particles are clearly formed in the gas-phase reaction of OH with CF₃(CF₂)₂CH=CH₂ at room temperature and atmospheric pressure.
- Secondary organic aerosol yield (SOA yield) was determined for the gas-phase reaction of OH with CF₃(CF₂)₂CH=CH₂ under different NO_x conditions, observing that the yield was higher at low NO_x concentration.