Understanding the Chemistry of Hydrofluoroolefin (HFO) Replacement Compounds: Cl Atom Kinetics and Adduct Formation

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Hydrofluorocarbons (HFCs) have been widely applied in various technologies, e.g. mobile air conditioning and foam blowing, as replacements for ozone depleting chlorofluorcarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). However, HFCs are, in general, potent greenhouse gases with high Global Warming Potentials (GWPs). Hydrofluoroolefins (HFOs) offer an alternative to their unsaturated predecessors where their high gas-phase reactivity leads to lower GWPs, thus, reducing their climate impacts. A thorough investigation of the atmospherically relevant chemical processing of these compounds is required in order to better understand their potential environmental impact.

Cl atom addition to the hydrofluoroolefins (HFOs) $CF_3CF=CH_2$ (2,3,3,3-tetrafluoropropene, HFO-1234yf) and (*Z*)-$CF_3CF=CHF$ (1,2,3,3,3-pentafluoropropene, HFO-1225ye) has previously been shown to, most likely, lead to the formation of a Cl-adduct that is semi-stable at 298 K or greater temperatures.[1,2] In this work, the Cl atom reaction with $CF_3CF=CH_2$ and (*Z*)-$CF_3CF=CHF$

$$Cl + CF_3CF=CH_2 \leftrightarrow CF_3CFClC^{\bullet}H_2 \quad (1a)$$

$$\leftrightarrow CF_3C^{\bullet}FCH_2Cl \quad (1b)$$

$$Cl + (Z)\text{-}CF_3CF=CHF \leftrightarrow CF_3CFClC^{\bullet}HF \quad (2a)$$

$$\leftrightarrow CF_3C^{\bullet}FCHFCl \quad (2b)$$

was studied over a range of temperature and pressure to further investigate the thermochemical parameters and reactivity of the Cl-adducts formed in reactions 1 and 2. Chlorine atoms were produced using pulsed laser photolysis of $(ClCO)_2$ or Cl_2 and its temporal profile measured using atomic resonance fluorescence (PLP-RF). Experiments were also performed with the addition of O_2 to the reaction mixture to determine the reactivity of the Cl-adducts with O_2. The results from this work are compared to earlier theoretical calculations from this group[1] and the indirect determinations from Kaiser *et al.*[2] for $CF_3CF=CH_2$.

References

(1) Papadimitriou, V.C.; Lazarou, Y.G.; Talukdar, R.J.; Burkholder, J.B. *J Phys. Chem. A.* **2011**, 115, 167-181.
(2) Kaiser, E.W.; Wallington, T.J. *J. Phys. Chem. A.* **2012**, ASAP.