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Atmospheric fate of hydrofluoroolefins, $C_xF_{2x+1}CH{=}CH_2$ (x = 1,2,3,4 and 6): Kinetics with Cl atoms and products

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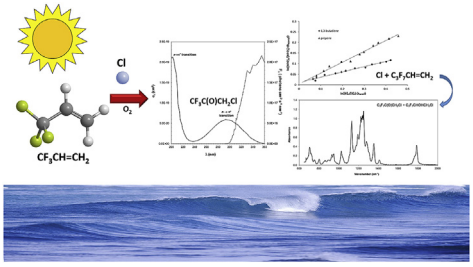
HIGHLIGHTS

- Rate coefficients for Cl-reaction with $C_xF_{2x+1}CH{=}CH_2$ (HFOs) at 298 K are determined.
- The atmospheric removal of HFOs initiated by Cl compete with OH reactions at dawn.
- Main reaction product: $C_xF_{2x+1}C(O)CH_2Cl$, i.e. reaction mechanism through Cl- addition to the double bond.
- Product $CF_3C(O)CH_2Cl$ reacts slowly with OH radicals, but UV photolysis is important.
- Minor products: $C_xF_{2x+1}CHO$, $C_xF_{2x+1}CHOHCH_2Cl$ and CF_2O.

GRAPHICAL ABSTRACT



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ABSTRACT

Rate coefficients for the gas-phase reactions of $C_xF_{2x+1}CH{=}CH_2$ (x = 1, 2, 3, 4 and 6) with Cl atoms were determined at (298 ± 2) K and (710 ± 5) Torr of air using a relative rate technique. Two experimental setups with simulation chambers were employed with Fourier Transform Infrared (FTIR) spectroscopy and Gas Chromatography coupled to Mass Spectrometry (GC-MS) as detection techniques. The Cl-rate coefficients obtained were (in 10^{-10} cm^3 $molecule^{-1}$ s^{-1}): (0.85 ± 0.11) for $CF_3CH{=}CH_2$, (1.11 ± 0.08) for $C_2F_5CH{=}CH_2$, (1.12 ± 0.18) for $C_3F_7CH{=}CH_2$, (0.97 ± 0.09) for $C_4F_9CH{=}CH_2$, and (0.99 ± 0.08) for $C_6F_{13}CH{=}CH_2$. Additionally, the gas-phase products were identified and quantified, when possible, by FTIR spectroscopy or GC-MS. The main reaction product was reported to be $C_xF_{2x+1}C(O)CH_2Cl$. The fluorinated species, $C_xF_{2x+1}CHO$ and $C_xF_{2x+1}C(O)CH_2Cl$, were identified. $CF_3C(O)CH_2Cl$ and CF_3CHO were found to be formed with molar yield of (69 ± 5)% and (9 ± 1)%, respectively. The global lifetime of the investigated $C_xF_{2x+1}CH{=}CH_2$ due to their Cl-reaction is more than 100 days so this route does not compete with the removal by OH radicals. This lifetime is long enough for $C_xF_{2x+1}CH{=}CH_2$ to be transported to remote areas where they can be degraded. However, at a local scale, in marine regions at dawn the removal of $C_xF_{2x+1}CH{=}CH_2$ is expected to occur in ca. 1 day. The atmospheric degradation of these hydrofluoroolefins by Cl atoms is not expected to be a source of bioaccumulative perfluorinated

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carboxylic acids, $C_xF_{2x+1}C(O)OH$. Additionally, the UV absorption cross sections of $CF_3C(O)CH_2Cl$ were determined together with the rate coefficient of the OH reaction by an absolute kinetic method at room temperature.

1. Introduction

Hydrofluoroolefins (HFOs), particularly $C_xF_{2x+1}CH{=}CH_2$, have been proposed as replacements for hydrofluorocarbons (HFCs) in many applications. For instance, the U.S. Environmental Protection Agency (EPA) has proposed 3,3,3-trifluoropropene ($CF_3CH{=}CH_2$, HFO-1243zf) as a replacement for CF_3CFH_2 (HFC-134a) in mobile air conditioning units (USEPA, 2010). Among other HFOs, 3,3,4,4,4-pentafluoro-1-butene ($C_2F_5CH{=}CH_2$, HFC-1345fz) is being considered as the new generation of foam expansion agents (Creazzo et al., 2007). Atmospheric degradation of $C_xF_{2x+1}CH{=}CH_2$ might without to be one of the sources of bioaccumulative and potentially toxic perfluorinated carboxylic acids (PFCAs, $C_xF_{2x+1}C(O)OH$) in remote regions, where they were detected in some species like fish and mammals (Moody et al., 2001, 2002; Martin et al., 2004). For that reason, before the widespread use of $C_xF_{2x+1}CH{=}CH_2$, an evaluation of their atmospheric persistence and the potential environmental effects of their degradation products is needed. The removal of $C_xF_{2x+1}CH{=}CH_2$ in the troposphere is mainly controlled by reaction with OH radicals (Orkin et al., 1997; Vésine et al., 2000; Sulbaek Andersen et al., 2005; Jiménez et al., 2014, 2016; González et al., 2015; Jiménez et al., 2016; González et al., 2016), while oxidation via Cl atoms can also be an important homogeneous loss process at dawn, not only in coastal or marine regions, but in mid-continental and urban areas as well (Tanaka et al., 2003; Thornton et al., 2010; Faxon and Allen, 2013). To our knowledge, at room temperature the kinetics of the reactions of Cl atoms with $CF_3CH{=}CH_2$, $C_2F_5CH{=}CH_2$, $C_4F_9CH{=}CH_2$ and $C_6F_{13}CH{=}CH_2$ have been performed in a pressure range from 9.1 to 760 Torr (Vésine et al., 2000; Sulbaek Andersen et al., 2005; Takahashi et al., 2007).

The product distribution for the Cl-reactions with $CF_3CH{=}CH_2$ (Nakayama et al., 2007), $C_4F_9CH{=}CH_2$ (Vésine et al., 2000) and $C_6F_{13}CH{=}CH_2$ (Vésine et al., 2000; Nakayama et al., 2007) has been determined in the absence and presence of NO_x by Fourier Transform Infrared (FTIR) spectroscopy. In these studies the main primary reaction product was suggested to be the halogenated ketones, $C_xF_{2x+1}C(O)CH_2Cl$. Nakayama et al. (2007) identified and quantified $CF_3C(O)CH_2Cl$, but $C_4F_9C(O)CH_2Cl$ and $C_6F_{13}C(O)CH_2Cl$ were not confirmed by Vésine et al. (2000). As a consequence, the atmospheric fate of $C_xF_{2x+1}C(O)CH_2Cl$ is not fully understood. As far as we know, only the kinetics at room temperature of the gas-phase reaction of Cl atoms with $CF_3C(O)CH_2Cl$ was reported by Nakayama et al. (2007) ($k = (5.63 \pm 0.66) \times 10^{-14}$ $cm^3 molecule^{-1} s^{-1}$). The rate coefficient for the Cl + $CF_3C(O)CH_2Cl$ reaction is too small to contribute to the atmospheric removal of this species. However, other degradation routes for $CF_3C(O)CH_2Cl$, such as OH reaction or UV photolysis, have not been investigated yet. These studies would help to assess the atmospheric fate of $CF_3C(O)CH_2Cl$, in particular, and by extension of $C_xF_{2x+1}C(O)CH_2Cl$.

No kinetic data or product studies are currently available for the reaction of Cl with $C_3F_7CH{=}CH_2$. The aim of this work is, therefore, to determine the rate coefficients for the reaction of Cl atoms with the series of HFOs ($C_xF_{2x+1}CH{=}CH_2$, where x = 1, 2, 3, 4 and 6) at atmospheric pressure and room temperature. Additionally to the kinetic experiments, the main gaseous products of the titled reactions in absence of NO_x were identified and quantified, when possible, in order to evaluate the role of these HFOs and their degradation products in the formation of PFCAs. Finally, the atmospheric fate of $CF_3C(O)CH_2Cl$, the major oxidation product of the $CF_3CH{=}CH_2$ + Cl reaction was investigated by determining the UV absorption cross sections between 210 and 360 nm and the rate coefficient of the $CF_3C(O)CH_2Cl$ + OH reaction at room temperature. The atmospheric implications of this study will be discussed.

2. Experimental systems

2.1. Relative kinetics and product studies in Cl-reactions

The experimental system used in this study has been presented in detail previously (Ballesteros et al., 2007, 2009; Ceacero-Vega et al., 2011; Ceacero-Vega et al., 2012), thus, it will be described briefly here.

The relative kinetic measurements and the detection of reaction products were performed in three different environmental chambers coupled to a FTIR spectrometer or a Gas Chromatography coupled to Mass Spectrometry (GC-MS) as detection techniques. The first one consists of a 16 L borosilicate glass cylinder reaction chamber, homogeneously surrounded by 4 UV–visible lamps (Philips TL-K 40 W, $\lambda = 300–450$ nm with $\lambda_{max} = 365$ nm), coupled to a Nexus Thermo Nicolet FTIR spectrometer equipped with a mercury cadmium telluride detector (MCT). The reactor is equipped with a White type multiple-reflection mirror system, with a total path length of 96 m, for in situ absorption monitoring of reactants and products in the IR spectral range 4000–650 cm^{-1}.

Chlorine atoms were produced by the broad-band UV–visible photolysis of Cl_2 in the bath gas (synthetic air). UV radiation was produced by the lamps homogeneously arranged around the outside of the reactors.

Two other smog chambers were used in this study: a Teflon bag of 200 L and a glass cylindrical reactor of 264 L. These reaction chambers were surrounded by 8 lamps emitting in the UV–visible region (Philips TL 40 W/05, $\lambda = 300–450$ nm with $\lambda_{max} = 365$ nm) and coupled to a Gas Chromatography (Thermo Electron Co., model Trace GC Ultra) attached to a Mass Spectrometer (Thermo Electron Co., model DSQ II) for reactant and product analysis. The experiments were carried out using the solid-phase microextraction sampling technique, SPME, with a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco). The coated fiber was inserted into the chamber and then exposed during 15 min (in consonance with a saturation curve previously determined) to the mixture of the reactor. After each experiment, the reaction chambers were cleaned out by repeated purge-pump cycles until the reactants and/or products were not detected.

For the three chambers, reactants were introduced directly into the cell by expansion from a glass manifold system (calibrated volume) and mixed with synthetic air at (298 ± 2) K and (710 ± 5) Torr of total pressure. Gas-phase concentrations in the reactor were calculated considering the gas partial pressure in a cylinder of known volume and the total volume of the reactor. Reaction mixtures consisted of 8.6–16.8 parts per million (ppm) of $C_xF_{2x+1}CH{=}CH_2$ (where x = 1, 2, 3, 4 and 6), 11.9–18.1 ppm of Cl_2 and 8.7–18.0 ppm of reference compound (propene, 1,3-butadiene and