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Atmospheric chemistry of $C_xF_{2x+1}CH{=}CH_2$ ($x = 1, 2, 4, 6$, and 8): Kinetics of gas-phase reactions with Cl atoms, OH radicals, and O_3

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Abstract

Long-path length FT-IR-smog chamber techniques were used to study the title reactions in 700 Torr of N_2 or N_2/O_2, diluent at 296 K. There was no discernable effect of C_xF_{2x+1}-group size on the reactivity of $C_xF_{2x+1}CH{=}CH_2$ towards Cl atoms and OH radicals. Values of $k(Cl + C_xF_{2x+1}CH{=}CH_2) = (9.07 \pm 1.08) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k(OH + C_xF_{2x+1}CH{=}CH_2) = (1.36 \pm 0.25) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} were measured. Ozone reacts more rapidly with $CF_3CH{=}CH_2$ than with larger members of the series; $k(O_3 + CF_3CH{=}CH_2) = (3.5 \pm 0.3) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} and $k(O_3 + C_xF_{2x+1}CH{=}CH_2) = (2.0 \pm 0.4) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} ($x \geq 2$). The atmospheric lifetime of $C_xF_{2x+1}CH{=}CH_2$ ($x \geq 2$) is approximately 8 days with 90% of removal occurring via reaction with OH and 10% via reaction with O_3.

Keywords: Atmospheric chemistry; Fluoroalkenes; Hydroxy radical

1. Introduction

Perfluorinated carboxylic acids (PFCAs, $C_xF_{2x+1}COOH$, where $x = 6$–12) have been observed in fish [1,2] and mammals [3] around the world. Long-chain perfluorinated acids have been shown to be bioaccumulative [4,5] and potentially toxic [6–8]. While there are no known natural sources of long-chain PFCAs, these compounds have been directly emitted to the environment via industrial processes. Such processes, include use of PFCAs and their salts as processing aids in the polymerization of fluoropolymers and in fire-fighting foams [1,9,10].

The observation of PFCAs in remote regions far from industrial sources and large population centers is puzzling, since PFCAs are not expected to be particularly mobile in the environment [11]. Among the direct emission pathways, that might partially account for observed PFCA loadings in the Arctic are the potential transport of PFCAs by marine aerosols [12] and the local use of PFCA containing materials, e.g. the historic use of fire-fighting foams in military installations in the Arctic. In addition, a portion of the observed PFCAs may originate from precursor substances which are transformed by atmospheric oxidation processes: potential PFCA precursors, include perfluorosulfonamide alcohols and fluorotelomer substances, such as fluorotelomer alcohols and olefins [13,14]. The relative contribution of direct sources and precursors to PFCAs identified in remote locations is not known at present.

Fluorotelomer acrylate monomer is a principal raw material used to make fluorotelomer-based polymeric products [15]. When manufactured, the monomer contains

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fluorotelomer alcohols or fluorotelomer olefins as a residual raw material impurity at levels up to a few hundred parts per million by weight. During industrial use, these residual alcohols and olefins are expected to be released to the air. Fluorotelomer alcohols, $C_xF_{2x+1}CH_2CH_2OH$ (x = 6, 8, 10, and 12), have previously been observed in air samples and suggested as a plausible source of PFCAs present in remote locations [16]. Although not so far reported to be found in air samples, atmospheric oxidation of fluorotelomer olefins, $C_xF_{2x+1}CH{=}CH_2$ (x = 8, 10, and 12) may also be a source of PFCAs. To assess the ability of $C_xF_{2x+1}CH{=}CH_2$ to survive long-range transport and hence contribute to the global PFCA budget, we have conducted a study of the atmospheric chemistry of fluorotelomer olefins. Specifically, we have studied the kinetics of the gas phase reactions of Cl atoms, OH radicals, and O_3 with $C_xF_{2x+1}CH{=}CH_2$ (x = 1, 2, 4, 6, and 8). Results are reported herein.

2. Experimental

The experiments were performed in a 140 liter Pyrex reactor interfaced to a Mattson Sirus 100 FT-IR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine:

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air:

$$CH_3ONO + h\nu \rightarrow CH_3O(\cdot) + NO \tag{2}$$

$$CH_3O(\cdot) + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

In the relative rate experiments, the following reactions take place:

$$Cl + \text{Reactant} \rightarrow \text{products} \tag{5}$$

$$Cl + \text{Reference} \rightarrow \text{products} \tag{6}$$

$$OH + \text{Reactant} \rightarrow \text{products} \tag{7}$$

$$OH + \text{Reference} \rightarrow \text{products} \tag{8}$$

It can be shown that:

$$\ln\left(\frac{[\text{Reactant}]_{t_0}}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} \ln\left(\frac{[\text{Reference}]_{t_0}}{[\text{Reference}]_t}\right) \tag{9}$$

where $[\text{Reactant}]_{t_0}$, $[\text{Reactant}]_t$, $[\text{Reference}]_{t_0}$, and $[\text{Reference}]_t$ are the concentrations of reactant and reference at times t_0 and t, and k_{Reactant} and $k_{\text{Reference}}$ are the rate constants for the reactant and the reference. Plots of $\ln([\text{Reactant}]_{t_0}/[\text{Reactant}]_t)$ versus $\ln([\text{Reference}]_{t_0}/[\text{Reference}]_t)$ should be linear, pass through the origin and have a slope of $k_{\text{Reactant}}/k_{\text{Reference}}$. The kinetics of the O_3 reaction were studied using an absolute rate method in which the pseudo first order loss of $C_xF_{2x+1}CH{=}CH_2$ was measured in the presence of excess O_3.

O_3 was produced from O_2 via silent electrical discharge using a commercial O_3 ozonizer. CH_3ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of N_2, or N_2/O_2 diluent at 296 ± 2 K.

Concentrations of reactants and products were monitored by FT-IR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. There was no observable (<2%) loss of any of the reactants or products in the present work. Unless stated otherwise, quoted uncertainties are 2 S.D. from least squares regressions.

3. Results and discussion

3.1. Relative rate study of *$k(Cl + C_xF_{2x+1}CH{=}CH_2)$*

The kinetics of reaction (10) were measured relative to those of reactions (11) and (12):

$$Cl + C_xF_{2x+1}CH{=}CH_2 \rightarrow \text{products} \tag{10}$$

$$Cl + C_2H_4 \rightarrow \text{products} \tag{11}$$

$$Cl + C_2H_2 \rightarrow \text{products} \tag{12}$$

Reaction mixtures consisted of 7.8–14.7 mTorr of $C_xF_{2x+1}CH{=}CH_2$, 82.2–100.4 mTorr of Cl_2, and either 14.3–30.2 mTorr of C_2H_4, or 5.4–8.5 mTorr of C_2H_2, in 700 Torr of air, or N_2, diluent. The observed loss of $C_xF_{2x+1}CH{=}CH_2$ versus those of the reference compounds is plotted in Fig. 1. As seen in Fig. 1, there was no discernable effect of the size of the C_xF_{2x+1}-group on reactivity of the $C_xF_{2x+1}CH{=}CH_2$ molecule. Accordingly, we analyze the entire set of $C_xF_{2x+1}CH{=}CH_2$ together. Linear least squares analysis of the data in Fig. 1 gives $k_{10}/k_{11} = 0.987 \pm 0.090$, and $k_{10}/k_{12} = 1.77 \pm 0.14$.

Using $k_{11} = (9.29 \pm 0.51) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [17] and $k_{12} = (5.07 \pm 0.34) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [17] gives $k_{10} = (9.17 \pm 0.98) \times 10^{-11}$ and $(8.97 \pm 0.93) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Indistinguishable values of k_{10} are obtained using the two different references. We choose to cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, hence $k_{10} = (9.07 \pm 1.08) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Vesine et al. [18] have reported $k(Cl + C_4F_9CH{=}CH_2) = (8.9 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $k(Cl + C_6F_{13}CH{=}$