

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

M.P. Sulbaek Andersen^a, O.J. Nielsen^a, A. Toft^b, T. Nakayama^c, Y. Matsumi^c,
R.L. Waterland^d, R.C. Buck^e, M.D. Hurley^f, T.J. Wallington^{f,*}

^a Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK 2100 Copenhagen, Denmark

^b University of Southern Denmark, Department of Chemistry, Campusvej 55, DK 5230 Odense M, Denmark

^c Solar-Terrestrial Environment Laboratory, Graduate School of Science, Nagoya University, Honohara 3-13, Toyokawa, Aichi 442 8507, Japan

^d DuPont Information and Computing Technologies, Central Research and Technology, P.O. Box 80320, Wilmington, DE 19880-0320, USA

^e DuPont Chemical Solutions Enterprise, Barley Mill Plaza 23, Wilmington, DE 19805, USA

^f Physical and Environmental Sciences Department, Ford Motor Company, 20000 Rotunda Drive, Mail Drop SRL-3083, Dearborn, MI 48121, USA

Received 29 April 2005; received in revised form 15 June 2005; accepted 16 June 2005

Available online 1 August 2005

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 $k(Cl + C_xF_{2x+1}CH=CH_2) = (9.07 \pm 1.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(OH + C_xF_{2x+1}CH=CH_2) = (1.36 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were measured. Ozone reacts more rapidly with $CF_3CH=CH_2$ than with larger members of the series; $k(O_3 + CF_3CH=CH_2) = (3.5 \pm 0.3) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(O_3 + C_xF_{2x+1}CH=CH_2) = (2.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($x \geq 2$). 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 .

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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

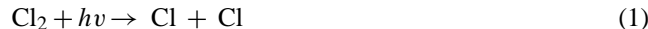
* Corresponding author. Tel.: +1 313 390 5574.

E-mail address: twalling@ford.com (T.J. Wallington).

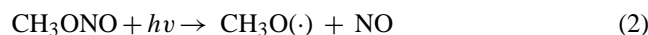
fluorotelomer alcohols or fluorotelomer olefins as a residual raw material impurity at levels up to a few hundred parts per million by weight. During industrial use, these residual alcohols and olefins are expected to be released to the air. Fluorotelomer alcohols, $C_xF_{2x+1}CH_2CH_2OH$ ($x=6, 8, 10,$ 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

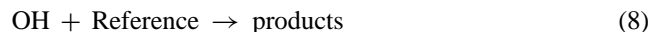
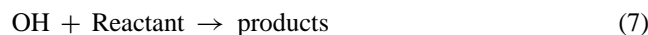
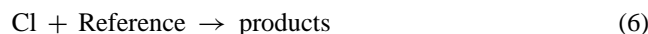
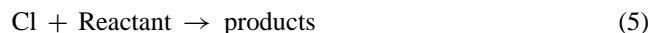
The experiments were performed in a 140 liter Pyrex reactor interfaced to a Mattson Sirius 100 FT-IR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular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



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



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



It can be shown that:

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

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 .

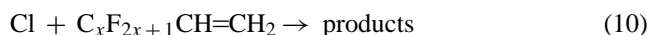
O_3 was produced from O_2 via silent electrical discharge using a commercial O_3 ozonizer. CH_3ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr 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):



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 $k_{11} = (9.29 \pm 0.51) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17] and $k_{12} = (5.07 \pm 0.34) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [17] gives $k_{10} = (9.17 \pm 0.98) \times 10^{-11}$ and $(8.97 \pm 0.93) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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 $k_{10} = (9.07 \pm 1.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Vesine et al. [18] have reported $k(Cl + C_4F_9CH=CH_2) = (8.9 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(Cl + C_6F_{13}CH=$

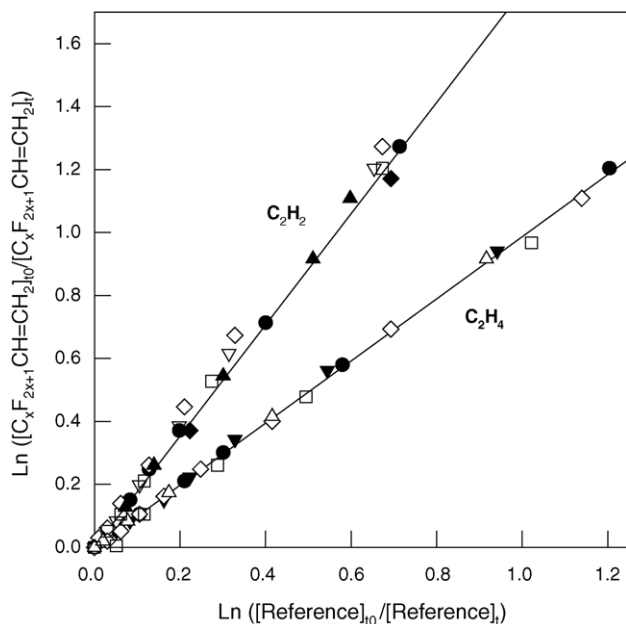
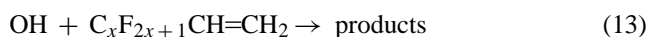


Fig. 1. Decay of $\text{CF}_3\text{CH}=\text{CH}_2$ (circles), $\text{C}_2\text{F}_5\text{CH}=\text{CH}_2$ (inverted triangles), $\text{C}_4\text{F}_9\text{CH}=\text{CH}_2$ (squares), $\text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2$ (triangles), and $\text{C}_8\text{F}_{17}\text{CH}=\text{CH}_2$ (diamonds) vs. C_2H_4 and C_2H_2 in the presence of Cl atoms in 700 Torr of either air (open symbols) or N_2 (filled symbols) at 296 ± 2 K.

CH_2) = $(9.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results of the present work are in good agreement with those of Vesine et al. [18]. The reactivity of Cl atoms towards $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ is indistinguishable from that towards $\text{CH}_2=\text{CH}_2$ [17] but is approximately a factor of 3 lower than towards $\text{CH}_3\text{CH}=\text{CH}_2$ [19]. As expected, replacement of the electron donating CH_3 -group by the electron withdrawing $\text{C}_x\text{F}_{2x+1}$ -group decreases the rate of electrophilic addition of Cl atoms to the $>\text{C}=\text{C}<$ double bond. A possible explanation for the similar reactivity of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CH}_2$ is that the deactivating influence of the electron withdrawing $\text{C}_x\text{F}_{2x+1}$ -group is countered by its stabilizing effect (increased number of degrees of freedom over which to spread the excess energy associated with C–Cl bond formation) in the initially formed Cl adduct.

3.2. Relative rate study of $k(\text{OH} + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2)$

The kinetics of reaction (13) were measured relative to reactions (14) and (15):



Initial reaction mixtures consisted of 14.4–93.0 mTorr of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$, 0–21 mTorr of NO, 88.3–96.4 mTorr of CH_3ONO , and 7.6–7.9 mTorr of C_2H_4 or 2.9–8.2 mTorr of C_2H_2 in 700 Torr total pressure of air diluent. Fig. 2 shows the loss of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ plotted versus loss of

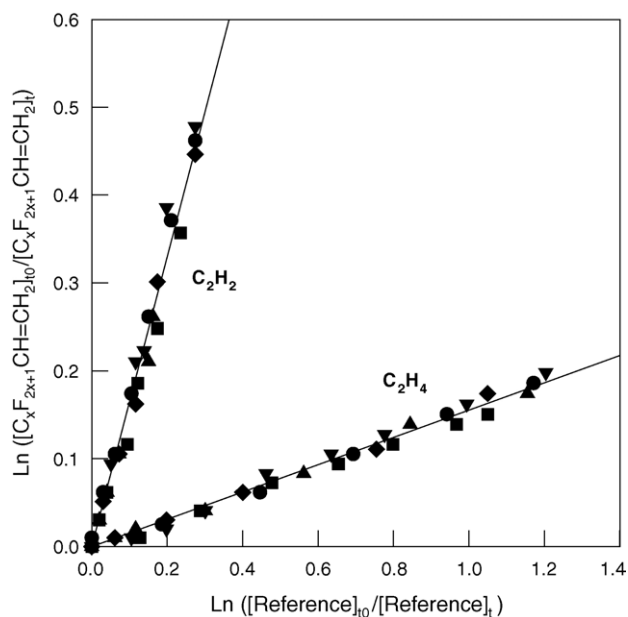


Fig. 2. Decay of $\text{CF}_3\text{CH}=\text{CH}_2$ (circles), $\text{C}_2\text{F}_5\text{CH}=\text{CH}_2$ (inverted triangles), $\text{C}_4\text{F}_9\text{CH}=\text{CH}_2$ (squares), $\text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2$ (triangles), and $\text{C}_8\text{F}_{17}\text{CH}=\text{CH}_2$ (diamonds) vs. C_2H_4 and C_2H_2 in the presence of OH radicals in 700 Torr of air at 296 ± 2 K.

the reference compounds. As with the Cl atom kinetic data presented in Section 3.1, it can be seen from Fig. 2 that there was no discernable effect of the size of the $\text{C}_x\text{F}_{2x+1}$ -group on reactivity of the $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ molecule. Accordingly, we analyze the entire set of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ together. Linear least squares analysis gives $k_{13}/k_{14} = 0.156 \pm 0.011$ and $k_{13}/k_{15} = 1.65 \pm 0.12$.

Using $k_{14} = (8.52 \pm 1.28) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [20] and $k_{15} = (8.45 \pm 0.85) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [21] gives $k_{13} = (1.33 \pm 0.22) \times 10^{-12}$ and $(1.39 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Indistinguishable values of k_{13} 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 $k_{13} = (1.36 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Orkin et al. [22] have reported $k(\text{OH} + \text{CF}_3\text{CH}=\text{CH}_2) = (1.54 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while Vesine et al. [18] have reported $k(\text{OH} + \text{C}_4\text{F}_9\text{CH}=\text{CH}_2) = (1.3 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{OH} + \text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2) = (1.5 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; our results are in good agreement with the previous studies. In contrast to the situation with Cl atom attack, the reactivity of OH radicals towards $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ is substantially (approximately a factor of 6) lower than towards $\text{CH}_2=\text{CH}_2$ and 22 times lower than towards $\text{CH}_3\text{CH}=\text{CH}_2$. As with Cl atoms, reaction with OH proceeds via electrophilic addition to the $>\text{C}=\text{C}<$ double bond. When compared to Cl atoms, OH radicals have a lower reactivity, are more discriminating, and hence are more sensitive to the presence of the electron withdrawing $\text{C}_x\text{F}_{2x+1}$ -substituents.

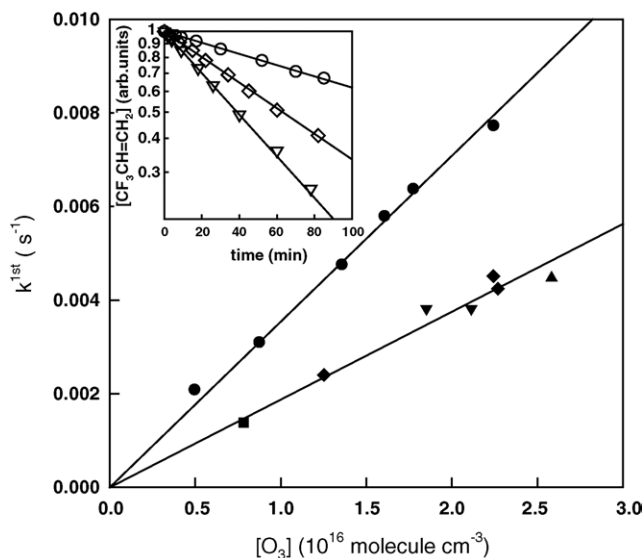


Fig. 3. Pseudo first order loss of $\text{CF}_3\text{CH}=\text{CH}_2$ (circles), $\text{C}_2\text{F}_5\text{CH}=\text{CH}_2$ (inverted triangles), $\text{C}_4\text{F}_9\text{CH}=\text{CH}_2$ (square), $\text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2$ (triangle), and $\text{C}_8\text{F}_{17}\text{CH}=\text{CH}_2$ (diamonds) vs. O_3 concentration. The insert shows typical decay plots for $\text{CF}_3\text{CH}=\text{CH}_2$ when exposed to 148 mTorr (circles), 395 mTorr (diamonds), or 679 mTorr (triangles) of O_3 .

3.3. Absolute rate study of $k(\text{O}_3 + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2)$

The kinetics of reaction (16) were studied by observing the decay of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ when exposed to ozone in the reaction chamber. Reaction mixtures consisted of 6.8–22.5 mTorr $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$, 14.3–43.2 mTorr cyclohexane, and 253–740 mTorr O_3 in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ via reaction with OH radicals formed in reaction (16). Variation of the cyclohexane concentration by a factor of 3 had no discernable effect on the observed decay of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ suggesting that loss via reaction with OH radicals is not a significant complication in the present work. The loss of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ followed pseudo first order kinetics in all experiments (see inset in Fig. 3):

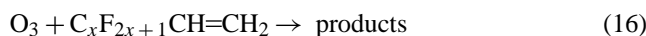
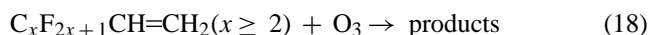
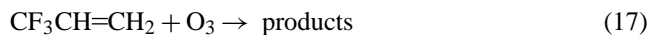


Fig. 3 shows a plot of the pseudo first order loss of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ versus O_3 concentration. The results obtained in the present work fall into two distinct groups. The smallest member of the series, $\text{CF}_3\text{CH}=\text{CH}_2$, had a distinctly greater reactivity towards O_3 than the larger members of the series. As evident from inspection of Fig. 3, increasing size of the fluorinated alkyl group from C_2F_5 to C_8F_{17} had no discernable impact on the reactivity of the molecule towards ozone. Hence, we choose to analyze the data in two sets: (i) $\text{CF}_3\text{CH}=\text{CH}_2$, and (ii) $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x \geq 2$). In the absence of O_3 , there was no observable loss (<2%) of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ on standing in the chamber for 60 min, and hence we choose to conduct a linear least squares analysis of the data in Fig. 3 with the intercept fixed at the origin.

The lines through the data give $k_{17} = (3.5 \pm 0.3) \times 10^{-19}$ and $k_{18} = (2.0 \pm 0.2) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In view of the relative few data points for $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x \geq 2$) in Fig. 3, we choose to quote $k_{18} = (2.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



It is of interest to compare and contrast the reactivity of O_3 towards fluoroalkenes [23] and alkenes. The reported rate constants for reactions of O_3 with propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-decene are indistinguishable and are approximately $1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [20]. In their reactions with O_3 , $\text{CF}_3\text{CH}=\text{CH}_2$ and $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x \geq 2$) are less reactive than their non-fluorinated counterparts by factors of 30 and 50, respectively. As with Cl atoms and OH radicals, reaction occurs by electrophilic addition of O_3 to the $>\text{C}=\text{C}<$ double bond. When compared to Cl atoms and OH radicals, O_3 has the lowest reactivity and hence is most sensitive to the presence of the electron withdrawing $\text{C}_x\text{F}_{2x+1}$ -substituent.

4. Implications for atmospheric chemistry

The present work improves our understanding of the atmospheric chemistry of fluorinated olefins of the general formula $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$. Cl atoms and OH radicals react with $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x=1, 2, 4, 6,$ and 8) with rate constants of $(9.07 \pm 1.08) \times 10^{-11}$ and $(1.36 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. O_3 reacts with $\text{CF}_3\text{CH}=\text{CH}_2$ with a rate constant of $(3.5 \pm 0.3) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and with $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x \geq 2$) with a rate constant of $(2.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reactivity of Cl atoms and OH radicals towards $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x=1, 2, 4, 6,$ and 8) and the reactivity of O_3 towards $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ ($x=2, 4, 6,$ and 8) does not depend on the size of the $\text{C}_x\text{F}_{2x+1}$ -group. Hence, we are able to generalize our results for $x \geq 2$; $k(\text{Cl} + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2) = (9.07 \pm 1.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{OH} + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2) = (1.36 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k(\text{O}_3 + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2) \text{ break} = (2.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The value of $k(\text{OH} + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2)$ derived above can be used to provide an estimate of the atmospheric lifetime of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$. Using a global weighted-average OH concentration of $1.0 \times 10^6 \text{ molecule cm}^{-3}$ [24] leads to an estimated lifetime of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ with respect to reaction with OH radicals of 8.5 days. Our value of $k(\text{O}_3 + \text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2)$ can be used to provide an estimate of the atmospheric lifetime of $\text{C}_x\text{F}_{2x+1}\text{CH}=\text{CH}_2$ with respect to reaction with O_3 . The global background concentration of O_3 is approximately 35 ppb [25] which leads to an estimated lifetime of 70 days.

The approximate nature of these lifetime estimates should be stressed; the average daily concentration of OH radicals and O₃ in the atmosphere varies significantly with both location and season [26]. The values above are estimates of global average lifetimes; local lifetimes could be different from those quoted above. C_xF_{2x+1}CH=CH₂ compounds will not undergo photolysis [22] and are not expected to be removed effectively by either wet or dry deposition. Cl atoms are not present in the atmosphere in sufficient quantity to impact the lifetime of C_xF_{2x+1}CH=CH₂. Hence, reaction with OH and O₃ are expected to be the major loss mechanism for these fluorinated olefins. The overall atmospheric lifetime of C_xF_{2x+1}CH=CH₂ ($x \geq 2$) is then expected to be 7.6 days with removal occurring approximately 90% via reaction with OH and 10% via reaction with O₃. The global average wind speed is 4 m s⁻¹ and in 7.6 days air masses can travel approximately 2000–3000 km. Following its release into the environment, it is expected that C_xF_{2x+1}CH=CH₂ will survive long-range transport in the atmosphere. There are three necessary conditions for C_xF_{2x+1}CH=CH₂ emissions to make a significant contribution to the perfluorocarboxylic acid burden observed in remote areas. First, C_xF_{2x+1}CH=CH₂ emissions need to be of a sufficient magnitude. Second, either C_xF_{2x+1}CH=CH₂ or its degradation products must survive long range transport. Third, C_xF_{2x+1}CH=CH₂ must degrade to give a significant perfluorocarboxylic acid yield. The present work shows that the second condition is met.

Acknowledgements

The Nagoya group thanks both Grants-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and also the Steel Industrial Foundation for the Advancement of Environmental Protection Technology for financial support. MPSA thanks the Danish National Research Agency for a research grant.

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