Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes

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Relative rate techniques were used to study the kinetics of the reactions of OH radicals with a homologous series of perfluorinated acids, $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$), in 700 Torr of air at 296 ± 2 K. For $n > 1$, the length of the $F(CF_2)_n$ group had no discernible impact on the reactivity of the molecule. For $n = 1$, $k(OH + F(CF_2)_nCOOH) = (9.35 \pm 2.08) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. For $n = 2-4$, $k(OH + F(CF_2)_nCOOH) = (1.69 \pm 0.22) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Dimerization constants for $2F(CF_2)_nCOOH = (F(CF_2)_nCOOH)_2$ were determined to be 0.32 ± 0.03 Torr^{-1}, 0.30 ± 0.03 Torr^{-1}, 0.41 ± 0.04 Torr^{-1}, and 0.46 ± 0.05 Torr^{-1} for $n = 1, 2, 3, 4$, respectively. Atmospheric lifetimes of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals are estimated to be approximately 230 days for $n = 1$ and 130 days for $n > 1$. Reaction with OH radicals is a minor atmospheric fate of $F(CF_2)_nCOOH$. The major atmospheric removal mechanism for $F(CF_2)_nCOOH$ is believed to be wet and dry deposition which probably occurs on a time scale of the order of 10 days.

1. Introduction

Perfluorinated carboxylic acids (PFCAs) of varying carbon chain-lengths have been observed in a suite of environmental matrixes from a variety of sources. Other than for trifluoroacetic acid (TFA),[1] no natural source of these PFCAs has been proposed, and it is probable they are anthropogenically derived. While the environmental fate, disposition, and persistence of TFA, the smallest of the PFCAs, has been the subject of numerous studies,[2] the source of the large amounts of TFA observed in the environment (particularly the oceans) is unknown.[3] TFA and PFCAs (e.g., with notation $F(CF_2)_nCOOH$, where $n = 1-12$), are minor products emitted to the atmosphere from thermolysis of fluoropolymers.[4] However, the thermolysis of fluoropolymers is unlikely to make a significant contribution to the observed global burden of PFCAs. Analysis of rainwater indicated the wide-spread occurrence of short-chain PFCAs ($n = 2$ through 7) at low (∼1 to 100 ng/L) levels.[5] Longer-chain PFCAs are bioaccumulative and were first discovered in fish downstream of a spill of aqueous film forming foam (AFFF).[3,6] Subsequent data from related surface waters suggest the spill was not the source of long PFCAs.[7] Long-chain PFCAs have also been observed in fish from the Great Lakes[8] and in arctic fish and mammals.[9]

As a class, the perfluorinated acids are highly persistent in the environment. PFCAs resist degradation via oxidation, hydrolysis, or reduction under biotic and abiotic conditions.[10] Although TFA has been observed to undergo biodegradation under engineered bioreactor conditions,[11] the importance of this process in the environment is unclear. The length of the carbon chain influences environmentally relevant physical properties such as vapor pressure, sorption, and bioaccumulation. For instance, each additional $-CF_2$ group in a homologous series of PFCAs ($n = 6-10$) results in an 8-fold increase of the bioconcentration potential in juvenile rainbow trout.[12,13]

Reaction with OH radicals offers a potential loss mechanism for long chain PFCAs in the environment. Unfortunately, while kinetic data are available for reaction of OH with TFA, there are no available data concerning the reactivity of longer chain perfluorinated carboxylic acids. To improve our understanding of the atmospheric fate of PFCAs we have conducted an experimental study of the kinetics of the reaction of OH with the first four members of the homologous series $F(CF_2)_nCOOH$. Atmospheric lifetimes with respect to reaction with OH are estimated and compared to the expected lifetimes with respect to removal via wet and dry deposition.

2. Experimental Section

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[14] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. OH radicals were produced by the photolysis of CH_3ONO in the presence of NO in air:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (1)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \quad (2)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (3)$$

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. OH radical kinetics are studied by irradiating CH_3ONO/NO/reactant/reference/air mixtures using UV fluorescent blacklamps. The relevant reactions in the system are (eqs 1−5):

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$$\mathrm{OH} + \mathrm{reactant} \rightarrow \mathrm{products} \tag{4}$$

$$\mathrm{OH} + \mathrm{reference} \rightarrow \mathrm{products} \tag{5}$$

It can be shown[15] that

$$\ln\left(\frac{[\mathrm{reactant}]t_0}{[\mathrm{reactant}]t}\right) = \frac{k_4}{k_5}\ln\left(\frac{[\mathrm{reference}]t_0}{[\mathrm{reference}]t}\right) \tag{I}$$

where [reactant]t_0, [reactant]t, [reference]t_0,and [reference]t are the concentrations of reactant and reference at times t_o and t, and k_4 and k_5 are the rate constants for reactions 4 and 5. Plots of ln([reactant]t_0/[reactant]t) versus ln([reference]t_0/[reference]t) should be linear, pass through the origin, and have a slope of k_4/k_5.

The reference compounds were monitored by FTIR spectroscopy using an infrared path length of 27 m, and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. The acids are liquids and were introduced into the chamber by transferring the vapor above the liquid into a calibrated volume. The contents of the calibrated volume were swept into the chamber using air. The acid concentrations in the chamber were calculated using the measured pressures of their vapor in the calibrated volumes.

Photolysis of CH_3ONO is the most widely used source of OH radicals in relative rate studies. However, CH_3ONO reacts with OH at a rate of approximately 3×10^{-13} cm^3 molecule^{-1} s^{-1},[16] scavenging OH radicals and making the loss of less reactive compounds (such as the PFCAs studied here) small and difficult to measure. A variation of the relative rate technique was used[17] in which the loss of the reactant was monitored indirectly by observing the formation of an oxidation product. The loss of the PFCA reactant can be calculated from the observed formation of its oxidation product, COF_2.[18] The OH-initiated oxidation of perfluorinated acids is expected to proceed via the following steps:

$$\mathrm{F(CF_2)_{\mathit{n}}COOH} + \mathrm{OH} \rightarrow \mathrm{F(CF_2)_{\mathit{n}}COO} + \mathrm{H_2O} \tag{6}$$

$$\mathrm{F(CF_2)_{\mathit{n}}COO} \rightarrow \mathrm{F(CF_2)_{\mathit{n}}} + \mathrm{CO_2} \tag{7}$$

$$\mathrm{F(CF_2)_{\mathit{n}}} + \mathrm{O_2} \rightarrow \mathrm{F(CF_2)_{\mathit{n}}O_2} \tag{8}$$

$$\mathrm{F(CF_2)_{\mathit{n}}O_2} + \mathrm{NO} \rightarrow \mathrm{F(CF_2)_{\mathit{n}}O} + \mathrm{NO_2} \tag{9}$$

$$\mathrm{F(CF_2)_{\mathit{n}-1}CF_2O} \rightarrow \mathrm{F(CF_2)_{\mathit{n}-1}} + \mathrm{COF_2} \tag{10}$$

Once the $F(CF_2)_n$ radical is formed, the reaction sequence of eqs 8−10 is repeated and the radical "unzips" by shedding COF_2 units until the CF_3 radical is formed which, in turn, is oxidized to give another COF_2 molecule.

$$\mathrm{CF_3} + \mathrm{O_2} \rightarrow \mathrm{CF_3O_2} \tag{11}$$

$$\mathrm{CF_3O_2} + \mathrm{NO} \rightarrow \mathrm{CF_3O} + \mathrm{NO_2} \tag{12a}$$

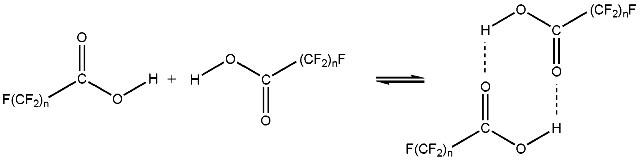
$$\mathrm{CF_3O_2} + \mathrm{NO} \rightarrow \mathrm{CF_3ONO_2} \tag{12b}$$

$$\mathrm{CF_3O} + \mathrm{NO} \rightarrow \mathrm{COF_2} + \mathrm{FNO} \tag{13}$$

The reaction of CF_3O_2 radicals with NO gives a yield of the nitrate, CF_3ONO_2, of 1.67% [unpublished results], i.e., $k_{12b}/(k_{12a} + k_{12b}) = 0.0167$. Evidence of low nitrate yield was observed by Giessing et al.,[19] who studied the reaction of $CF_3CF_2CF_2O_2$ with NO and concluded that the nitrate yield from the reaction of NO with $F(CF_2)_nO_2$ ($n = 1, 2, 3$) was less than 5%. Assuming that the nitrate yields in reaction 9 are also 1.67%, then for the perfluorinated acids $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$) the expected COF_2 yields are 98%, 193%, 290%, and 384%, respectively. COF_2 is readily detected by its absorption features at 774 and 1850−2000 cm^{-1}. Reference compounds were monitored using absorption features over the following wavenumber ranges: C_2H_4, 850−1050 cm^{-1}; and C_2H_2, 670−800 cm^{-1}. Initial concentrations of the gas mixtures for the relative rate experiments were 8−363 mTorr of $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$), 2−10 mTorr of the reference compounds (C_2H_2 or C_2H_4), 100−232 mTorr of CH_3ONO, and 10−25 mTorr of NO in 700 Torr of air diluent. All experiments were performed at 296 K. Reagents were obtained from commercial sources at purities >99% and were subjected to repeated freeze−pump−thaw cycling before use. Quoted uncertainties in the present report are, unless stated otherwise, 2 standard deviations from regression analyses.

3. Results

3.1. Determination of the Gas-Phase Dimerization Constant for $F(CF_2)_nCOOH$. Perfluorinated acids are known to form cyclic dimers[20−22]



and the observed pressure of $F(CF_2)_nCOOH$ vapor is expressed as

$$P_{\mathrm{obs}} = P_{\mathrm{M}} + P_D = P_{\mathrm{M}} + K_{\mathrm{d}}P_{\mathrm{M}}^{\ 2} \tag{II}$$

where P_M is the pressure of the monomer, P_D is the pressure of the dimer, and K_d is the dimerization constant. If dimerization occurs in the calibrated volume and the dimer dissociates upon expansion into the chamber, the acid concentration in the chamber will be higher than calculated, assuming only the monomer in the calibrated volume. To correct for dimer formation in the calibrated volume, the dimerization constant was determined for the perfluorinated acids, $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$). For the dimerization constant measurements, perfluorinated acid vapor was introduced into a small cell with a diameter of 4.5 cm and a length of 17.75 cm, filled to 700 Torr total pressure with nitrogen, placed in the IR beam, and the FTIR spectrum acquired. This procedure was repeated using different pressures of the acid vapor. As expected, the fraction of the acid present as the dimer increased as the concentration of acid was increased. Since the monomer and dimer are present in different relative amounts in spectra acquired using different concentrations of acid, the monomer and dimer spectra can be separated and quantified. Figure 1 shows the carbonyl region of the IR spectrum for the $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$) monomers and dimers. Absorption cross sections for the carbonyl feature of the acid monomers and dimers are given in Table 1.

From eq II, a plot of P_D vs $P_M^{\ 2}$ is expected to be linear, pass through the origin, and have a slope that is the dimerization constant, K_d. Figure 2 shows this plot for $F(CF_2)_4COOH$. The line through the data in Figure 2 is a linear least-squares fit which gives $K_d = 0.46 \pm 0.05$ Torr^{-1}. This procedure was repeated for the other perfluorinated acids, $F(CF_2)_nCOOH$ ($n = 1, 2, 3$). The dimerization constants were determined to be

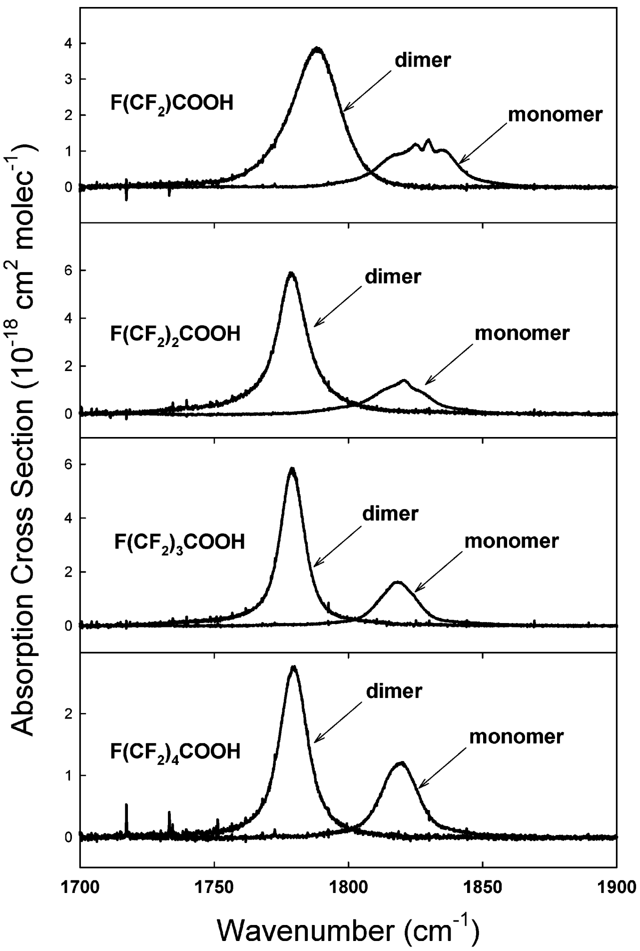


Figure 1. IR absorption cross section of carbonyl feature of $F(CF_2)_n$-COOH (n = 1, 2, 3, 4). The solid line is the monomer and the broken line is the dimer.

0.32 ± 0.03 Torr^{-1}, 0.30 ± 0.03 Torr^{-1}, and 0.41 ± 0.04 Torr^{-1} for FCF_2COOH, $F(CF_2)_2COOH$, and $F(CF_2)_3COOH$, respectively. These dimerization constants were used to account for dimer formation in our calibrated volume during the introduction of perfluorinated acids into the chamber. The vapor-phase dimerization constant for CF_3COOH at 298 K has been reported to be $K_d = 0.27 \pm 0.02$ Torr^{-1} by Møgelberg et al.,[23] $K_d = 0.30 \pm 0.02$ Torr^{-1} by Christian and Stevens,[21] and 0.45 Torr^{-1} by Meller et al.[24] The result obtained in the present work is consistent with the previous determination in this laboratory[23] and with that of Christian and Stevens,[21] but is significantly lower than the measurement by Meller et al.[24]

3.2. Relative Rate Study of the Reaction of OH Radicals with CF_3COOH. The reactivity of OH radicals toward CF_3COOH was studied relative to reactions 15 and 16.

$$OH + CF_3COOH \rightarrow \text{products} \qquad (14)$$

$$OH + C_2H_2 \rightarrow \text{products} \qquad (15)$$

$$OH + C_2H_4 \rightarrow \text{products} \qquad (16)$$

Figure 3 shows the loss of CF_3COOH, as calculated from the formation of COF_2, assuming the COF_2 yields discussed in section 2, versus loss of the reference compounds following the UV irradiation of CF_3COOH/reference/CH_3ONO/NO mixtures in air. The lines through the data in Figure 3 are linear least-squares fits to the data which give values of $k_{14}/k_{15} = 0.103 \pm 0.017$ and $k_{14}/k_{16} = 0.0116 \pm 0.0012$. Using $k_{15} = 8.45 \times 10^{-13}$ [25] and $k_{16} = 8.66 \times 10^{-12}$ [26] we derive $k_{14} = (8.70 \pm 1.44) \times 10^{-14}$ and $(1.00 \pm 0.11) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Within the experimental uncertainties, consistent results were obtained in experiments conducted using two different reference compounds. We choose to cite a final value for k_{14} which is the average of the two determinations together with error limits which encompass the extremes of the individual determinations. Hence, $k_{14} = (9.35 \pm 2.08) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

There are two previous studies with which we can compare our results. Møgelberg et al.[23] measured $k(OH + CF_3COOH) = (1.6 \pm 0.4) \times 10^{-13}$ at 315 K using an absolute rate pulse radiolysis technique and $k(OH + CF_3COOH) = (1.7 \pm 0.5) \times 10^{-13}$ at 296 K using a relative rate technique. Carr et al.[27] used a relative rate method to measure $k(OH + CF_3COOH) = (1.2 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. The result from the present study is in agreement, within the experimental uncertainties, with the study of Carr et al.[27] but is somewhat lower than the results reported by Møgelberg et al. In their pulse radiolysis experiments Møgelberg et al. used high concentrations of CF_3COOH (up to 15 mbar) and had to apply large corrections (up to 50%) to the data measured at 315 K to account for the presence of dimer. In the correction procedure, it was assumed that the dimer was unreactive toward OH radicals. The difference between the results from the present work and the pulse radiolysis study by Møgelberg et al. suggests either that the dimer is reactive to some degree or that the equilibrium constant used by Møgelberg et al. overestimated the level of dimer present at 315 K, or both.

As noted previously by Møgelberg et al.[23] and Carr et al.,[27] loss of $CF_3C(O)OH$ by reaction with CF_3O radicals is a potential complication in their relative rate studies. The present work differs from the two previous relative rate studies in one important respect; NO was present in the reaction mixtures in this work at levels sufficient to scavenge the CF_3O radicals. Additional loss of $CF_3C(O)OH$ via reaction with CF_3O may explain why the $k(OH + CF_3COOH)$ values obtained in the previous relative rate studies[23,27] lie somewhat above the value reported herein.

3.3. Relative Rate Study of the Reaction of OH Radicals with $F(CF_2)_nCOOH$ (n = 2, 3, 4). The reactivity of OH radicals toward $F(CF_2)_nCOOH$ (n = 2, 3, 4) was studied relative to reactions 15 and 16.

$$OH + F(CF_2)_nCOOH \rightarrow \text{products} \qquad (17)$$

Figure 4 shows the loss of $F(CF_2)_nCOOH$ (n = 2, 3, 4), as calculated from COF_2 formation assuming the COF_2 yields mentioned above, versus loss of the reference compounds on exposure to OH radicals. Experiments were performed in which the reactivity of OH radicals with $F(CF_2)_2COOH$, $F(CF_2)_3COOH$, and $F(CF_2)_4COOH$ were measured relative to the reactivity of C_2H_2 and C_2H_4. As seen in Figure 4, there was no discernible difference in the reactivity of the three perfluorinated acids. The lines through the data in Figure 4 are linear least-squares fits to the combined data sets which give values of $k_{17}/k_{15} = 0.197 \pm 0.022$ and $k_{17}/k_{16} = 0.0198 \pm 0.0014$. Using $k_{15} = 8.45 \times 10^{-13}$ [25] and $k_{16} = 8.66 \times 10^{-12}$ [26] we derive $k_{17} = (1.66 \pm 0.19) \times 10^{-13}$ and $(1.71 \pm 0.12) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Results obtained using the two different reference compounds were, within the experimental uncertainties, indistinguishable. The fact that consistent values of k_{17} were derived from experiments using different references suggests the absence of significant systematic errors associated with the choice of reference rate constants. In light of the small nitrate yields, k_{17} is not sensitive to uncertainties in such yields. Finally,

TABLE 1: IR Absorption Cross Section Data for $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$) Monomers and Dimers

	wavenumber (cm^{-1})	absorption cross section (cm^2 $molecule^{-1}$)	integrated absorption cross section 1700−1900 cm^{-1} (cm^2 $molecule^{-1}$ cm^{-1})
FCF_2COOH (monomer)	1830	1.31×10^{-18}	3.88×10^{-17}
FCF_2COOH (dimer)	1788	3.81×10^{-18}	9.73×10^{-17}
$F(CF_2)_2COOH$ (monomer)	1821	1.39×10^{-18}	3.48×10^{-17}
$F(CF_2)_2COOH$ (dimer)	1779	5.90×10^{-18}	1.17×10^{-16}
$F(CF_2)_3COOH$ (monomer)	1819	1.60×10^{-18}	3.50×10^{-17}
$F(CF_2)_3COOH$ (dimer)	1779	5.84×10^{-18}	8.96×10^{-17}
$F(CF_2)_4COOH$ (monomer)	1819	1.19×10^{-18}	2.40×10^{-17}
$F(CF_2)_4COOH$ (dimer)	1779	2.72×10^{-18}	4.55×10^{-17}

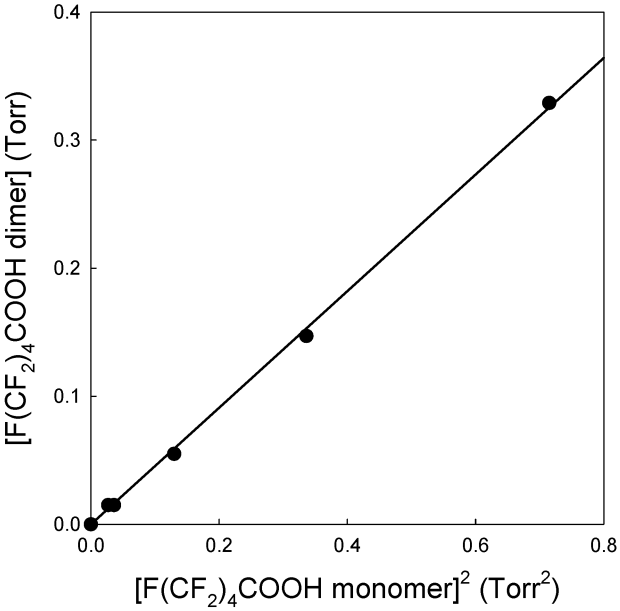


Figure 2. Formation of the C_4F_9COOH dimer as a function of the square of the C_4F_9COOH monomer pressure. The slope is the dimerization constant, $K_d = 0.45 \pm 0.05$ $Torr^{-1}$.

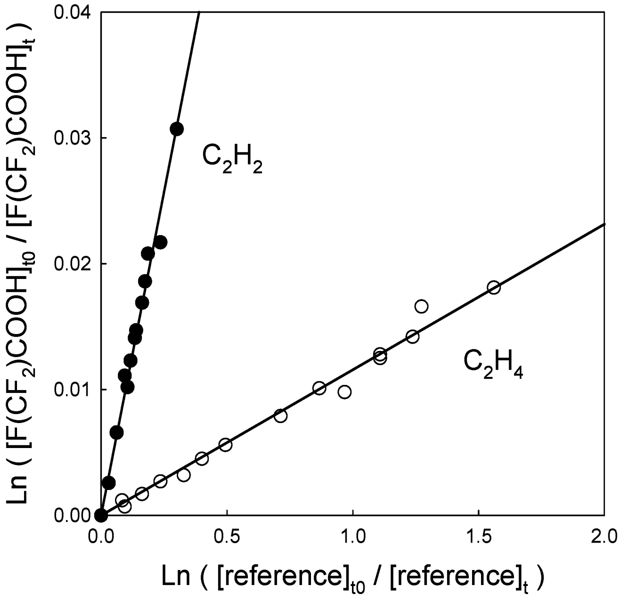


Figure 3. Loss of CF_3COOH versus C_2H_2 (filled) and C_2H_4 (open) following exposure to OH radicals in 700 Torr of N_2 diluent at 296 ± 2 K.

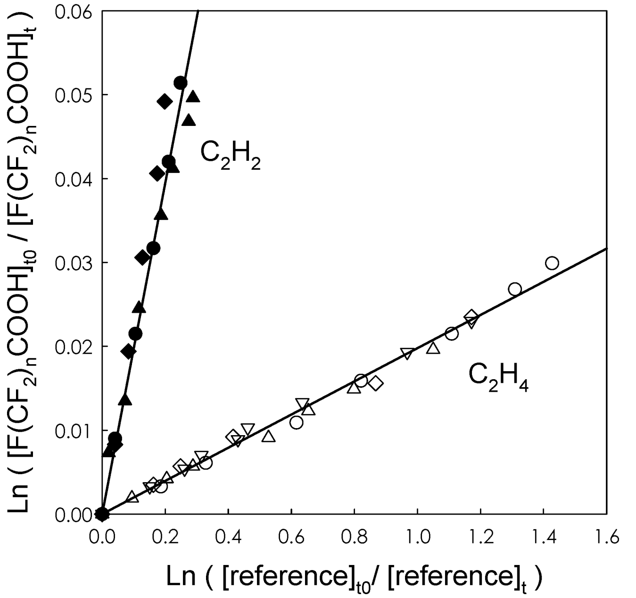


Figure 4. Loss of $F(CF_2)_nCOOH$ (circles, $n = 2$; diamonds, $n = 3$; triangles, $n = 4$) versus C_2H_2 (filled) and C_2H_4 (open) following exposure to OH radicals in 700 Torr of air diluent at 296 ± 2 K.

corrections of 15−60% were applied to account for dimerization of the acids in the calibrated volumes; indistinguishable values of k_{17} were obtained, suggesting the absence of significant uncertainties associated with the dimerization correction methodology. We choose to cite a final value for k_{17} which is the average of the two determinations together with error limits which encompass the extremes of the individual determinations. Hence, $k_{17} = (1.69 \pm 0.22) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. There have been no previous studies of the reactions of OH atoms with $F(CF_2)_nCOOH$ ($n > 1$).

4. Atmospheric Implications

The values of $k(OH + F(CF_2)_nCOOH)$ measured here can be used to provide an estimate of the atmospheric lifetime of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to reaction with OH radicals of 5.99 years[28] and a rate constant for the CH_3CCl_3 + OH reaction of 1.0×10^{-14} cm^3 $molecule^{-1}$ s^{-1} [29] leads to an estimate of the atmospheric lifetime of CF_3COOH of $(1.0 \times 10^{-14})/(9.35 \times 10^{-14}) \times 5.99 \times 365 \approx 230$ days. Similarly, the estimated atmospheric lifetime of $F(CF_2)_nCOOH$ ($n = 2, 3, 4$) is $(1.0 \times 10^{-14})/(1.69 \times 10^{-13}) \times 5.99 \times 365 \approx 130$ days. The optimal temperature for such a scaling analysis is 272 K[30] (rather than 296 K used here) but we do not have any data for k_{17} at 272 K. By analogy to other fluorinated organics,[31] the temperature dependence of the reaction of OH radicals with $F(CF_2)_nCOOH$ is expected to be similar to that for reaction with CH_3CCl_3. Hence, the use of 296 K rather than 272 K is not expected to have any material impact on the estimated atmospheric lifetimes. The approximate nature of the atmospheric lifetime estimates provided here should be stressed. The average daily concentration of OH radicals in the atmosphere varies significantly with both location and season.[32] The estimates presented here are for the global average lifetime with respect to reaction with OH radicals.

The atmospheric lifetime of perfluorinated acids depends not only on gas-phase reactivity, but also on the rate of wet and dry deposition. The key physical property controlling the deposition of perfluorinated acids is the Henry's Law Constant (K_H), and this has only been determined for TFA.[33] A quantitative estimation of the atmospheric removal processes for TFA has been conducted previously[34,35] and, based on its effectively low K_H of $\sim$1.0 e^{-5} Pa m^3 mol^{-1} (assuming $pK_a \sim 0.25$), it was concluded that TFA would be removed from the atmosphere at a rate similar to HNO_3, which has a lifetime of 9 days with respect to wet deposition, and 10−30 days with respect to dry deposition[34] (760 Torr = 101.3 kPa). Therefore, any gas-phase reactions of TFA with OH radicals are of minor importance, as previously discussed.[34,35] Although the longer chain perfluorinated acids (C3−C5) are more reactive than TFA toward OH radicals, their atmospheric fate will still be dominated by wet and dry deposition.

Although wet deposition was predicted to be more important than dry deposition for TFA,[34,35] recent environmental field measurements[36] suggest that wet and dry deposition are of approximately equal importance. In the absence of field measurements and with sparse physical property data, it is difficult to quantify the relative importance of wet and dry deposition for longer chain perfluorinated acids. In general terms, longer perfluorinated acids are less water soluble and less volatile than TFA. Lower solubility and lower volatility have opposite and hence offsetting effects on K_H. For gas-phase acids, we argue below that the importance of wet deposition will decrease as the perfluorinated chain-length increases, but that the relative importance of wet and dry deposition in the atmosphere will depend on the extent of gas-particle partitioning.

As the length of the perfluorinated chain increases, the molecule becomes more hydrophobic[37,38] and its water solubility diminishes. For example, whereas TFA is miscible with water, the water solubility of perfluorooctanoic acid is 3.4 g L^{-1}.[39] In terms of K_H, this effect of decreasing water solubility is only partially offset by the corresponding decrease in vapor pressure,[37,38] and the overall effect will be that K_H increases with increased perfluorinated chain-length. For example, using the vapor pressure for perfluoroheptanoic acid (53 Pa at 25 °C[40]), and the water solubility of perfluorooctanoic acid, K_H is calculated to be 6.5 Pa m^3 mol^{-1}. This partitioning coefficient is orders of magnitude larger than for TFA, indicating a wet deposition lifetime on the order of hundreds of years.[41,42] Assuming then that K_H increases linearly as the perfluorinated chain-length increases, it is apparent that the importance of direct wet deposition will decrease for longer chain acids.

Assessment of the importance of wet deposition is complicated by the fact that because of their decreased vapor pressure, larger perfluorinated acids will partition increasingly onto atmospheric particles.[43] The mean particle fraction for TFA has been reported to be 30% and, as noted for other carboxylic acids,[44] adsorption on particles probably plays an important role in the atmospheric fate of large PFCAs. Although long perfluorinated acids may not be removed by direct gas-precipitation partitioning, particle-associated perfluorinated acids would be effectively washed out by precipitation events. On average, the atmospheric residence time of particles due to wet washout and dry deposition is of the same general magnitude.[45] If perfluorinated acids are present exclusively on particles, the rate of wet deposition via particle washout could be comparable to that of dry deposition. The importance of wet and dry deposition for the perfluorinated acids will depend largely on the extent of particle adsorption.

The present work serves to clarify our understanding of the fate of gas-phase perfluorinated carboxylic acids in the atmosphere. From the present work we reach the following conclusions. First, reaction of TFA with OH radicals occurs with a rate constant of $(9.35 \pm 2.08) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. Second, longer chain perfluoro carboxylic acids react with OH with rate constants of $(1.69 \pm 0.22) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Third, the atmospheric lifetimes of TFA and longer-chain PFCAs with respect to reaction with OH radicals in the gas phase are approximately 230 and 130 days, respectively. Finally, the major atmospheric loss mechanism of PFCAs is dry and wet (particle mediated) deposition which occur on a time scale which is probably of the order of 10 days. Reaction with OH is a minor atmospheric loss mechanism for perfluorinated carboxylic acids.

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