Atmospheric Chemistry of n-$C_xF_{2x+1}CHO$ ($x = 1, 2, 3, 4$): Fate of n-$C_xF_{2x+1}C(O)$ Radicals

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Smog chamber/FTIR techniques were used to study the atmospheric fate of n-$C_xF_{2x+1}C(O)$ ($x = 1, 2, 3, 4$) radicals in 700 Torr O_2/N_2 diluent at 298 ± 3 K. A competition is observed between reaction with O_2 to form n-$C_xF_{2x+1}C(O)O_2$ radicals and decomposition to form n-C_xF_{2x+1} radicals and CO. In 700 Torr O_2/N_2 diluent at 298 ± 3 K, the rate constant ratio, $k(n\text{-}C_xF_{2x+1}C(O) + O_2 \rightarrow n\text{-}C_xF_{2x+1}C(O)O_2)/k(n\text{-}C_xF_{2x+1}C(O) \rightarrow n\text{-}C_xF_{2x+1} + CO) = (1.30 \pm 0.05) \times 10^{-17}$, $(1.90 \pm 0.17) \times 10^{-19}$, $(5.04 \pm 0.40) \times 10^{-20}$, and $(2.67 \pm 0.42) \times 10^{-20}$ cm^3 $molecule^{-1}$ for $x = 1, 2, 3, 4$, respectively. In one atmosphere of air at 298 K, reaction with O_2 accounts for 99%, 50%, 21%, and 12% of the loss of n-$C_xF_{2x+1}C(O)$ radicals for $x = 1, 2, 3, 4$, respectively. Results are discussed with respect to the atmospheric chemistry of n-$C_xF_{2x+1}C(O)$ radicals and their possible role in contributing to the formation of perfluorocarboxylic acids in the environment.

1. Introduction

Long-chain perfluorocarboxylic acids (PFCAs, n-C_xF_{2x+1}-COOH where $x \geq 6$) have been observed in fauna from the Great Lakes[1] and the Arctic.[2] PFCAs are not degraded via oxidation, hydrolysis, or reduction under biotic and abiotic conditions.[3] They are bioaccumulative when the perfluorinated chain is more than 6 carbons in length and are found in human blood.[4,5] Perfluorooctanoic acid (PFOA) is potentially toxic,[6] and the health effects of long-term exposure are under investigation. Other than for trifluoroacetic acid (TFA),[7] no natural source of PFCAs has been proposed. Two independent and distinctly different theories have been advanced to explain the presence of PFCAs in biota in remote regions: (1) the presence of widely distributed precursor compounds (presumably of anthropogenic origin) in the atmosphere that degrade to give PFCAs, which then undergo wet and dry deposition; and (2) the transport of PFCAs by ocean currents to remote locations and then by sea salt aerosol to inland locations.[8]

Support for the first theory comes from a recent atmospheric modeling study which reported that the atmospheric degradation of fluorotelomer alcohols ($C_xF_{2x+1}CH_2CH_2OH$ [$x = 2, 4, 6, ...$]) appears to be a significant global source of perfluorocarboxylic acids.[9] The atmospheric oxidation of $C_xF_{2x+1}CH_2CH_2OH$ gives $C_xF_{2x+1}CHO$.[10−13] There are several chemical mechanisms by which $C_xF_{2x+1}CHO$ can be converted into PFCAs. Two mechanisms are germane to the present investigation. First, oxidation of $C_xF_{2x+1}CHO$ to $C_xF_{2x+1}C(O)O_2$ radicals followed by reaction with HO_2 radicals to give $C_xF_{2x+1}C(O)OH$. Second, oxidation of $C_xF_{2x+1}CHO$ to $C_xF_{2x+1}O_2$ radicals, reaction of $C_xF_{2x+1}O_2$ with CH_3O_2 radicals to give $C_xF_{2x+1}OH$, decomposition of $C_xF_{2x+1}OH$ to $C_{x-1}F_{2x-1}C(O)F$, and hydrolysis of $C_{x-1}F_{2x-1}C(O)F$ to give $C_{x-1}F_{2x-1}C(O)OH$.[14]

Formation of $C_xF_{2x+1}C(O)O_2$ in the first mechanism involves the following reactions:

$$C_xF_{2x+1}CHO + OH \rightarrow C_xF_{2x+1}C(O) + H_2O \quad (1)$$

$$C_xF_{2x+1}C(O) + O_2 + M \rightarrow C_xF_{2x+1}C(O)O_2 + M \quad (2)$$

In our previous work[15−18] we assumed that, in air, the sole fate of the perfluoroacyl radical is reaction with oxygen to form the perfluoroacyl peroxy radical. The perfluoroacyl peroxy radical then reacts with other peroxy radicals or NO to form alkoxy radicals, which eliminate CO_2 to form perfluoroalkyl radicals. In a recent study of the reaction of Cl atoms with C_3F_7-CHO and $C_6F_{13}CHO$,[19] CO was observed as a primary product. The formation of CO as a primary product suggests that the reaction of the perfluoroacyl radical with oxygen competes with the decomposition of the perfluoroacyl radical.

$$C_xF_{2x+1}C(O) + M \rightarrow C_xF_{2x+1} + CO + M \quad (3)$$

In fact, this is consistent with previous studies that showed that halogenated acetyl radicals either decompose or react with oxygen.[20−22]

Since reaction of perfluoroacyl peroxy radicals with HO_2 has been shown to be a source of perfluorocarboxylic acid,[16,18] it is important to understand the chemical pathways that affect the formation of perfluoroacyl peroxy radicals in the atmosphere. The goal of the present work was to determine the importance of the decomposition channel and assess its impact on the formation of perfluorocarboxylic acids.

2. Experimental Section

The apparatus and experimental techniques used in this work are described elsewhere.[23,24] Experiments were performed in a

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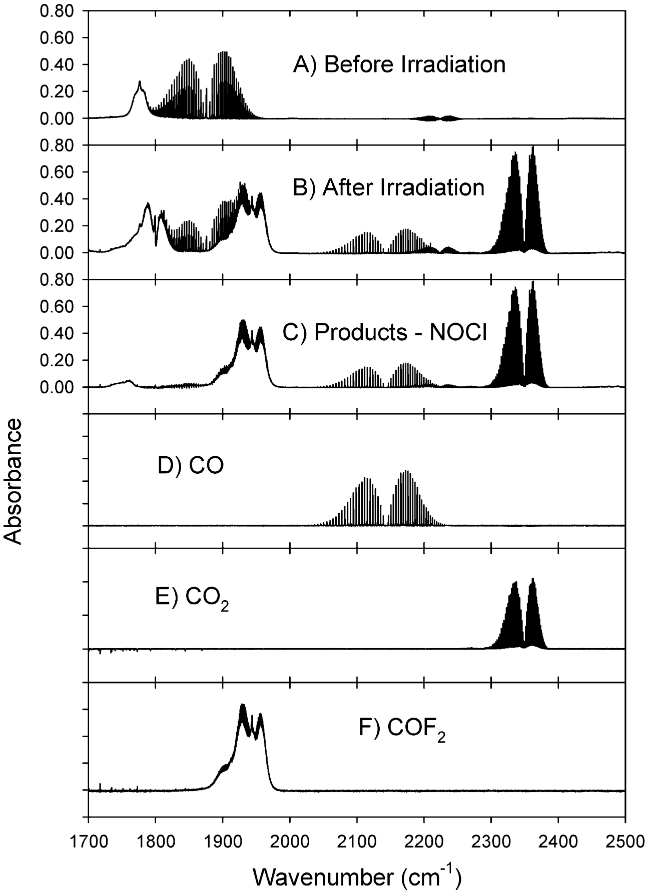

Figure 1. IR spectra obtained before (A) and after (B) a 4-min irradiation of a mixture of 14.3 mTorr C_2F_5CHO, 29.4 mTorr NO, 100 mTorr Cl_2, and 100 Torr O_2 pressurized to 700 Torr with N_2. The consumption of C_2F_5CHO was 34%. (C) The product spectrum with the IR features of NOCl removed. (D, E, F) Reference spectra of CO, CO_2, and COF_2, respectively.

140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR 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.

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (4)$$

$C_xF_{2x+1}C(O)$ ($x = 1, 2, 3, 4$) radicals were generated by the irradiation of $C_xF_{2x+1}CHO/Cl_2$ mixtures in 700 Torr of O_2/N_2 diluent gas.

$$C_xF_{2x+1}CHO + Cl \rightarrow C_xF_{2x+1}C(O) + HCl \qquad (5)$$

The perfluoroaldehydes were prepared by dehydration of the perfluoroaldehyde hydrates. The perfluoroaldehydes, C_xF_{2x+1}-CHO ($x = 1, 2$), were synthesized by the dropwise addition of 10 g of the perfluoroaldehyde hydrate into a heated flask (≈60 °C) containing 25 g of P_2O_5. Nitrogen gas was flowed slowly (≈20 cm^3 min^{-1}) over the heated hydrate/aldehyde mixture and through a liquid nitrogen trap where the aldehydes were collected. The perfluoroaldehydes, $C_xF_{2x+1}CHO$ ($x = 3, 4$), were synthesized by mixing 10 g of the solid perfluoroaldehyde hydrate, $C_xF_{2x+1}CH(OH)_2$ ($x = 3, 4$), with 25 g of P_2O_5, heating the mixture, and flowing nitrogen gas through the apparatus to collect the perfluoroaldehyde in a liquid nitrogen trap. No impurities were observed during IR analysis. Linear (n-$C_xF_{2x+1}CHO$) isomers were studied in the present work; for simplicity we refer to these compounds as $C_xF_{2x+1}CHO$. The perfluoroaldehyde reagents were stored in glass vials which were immersed in liquid nitrogen. They were introduced into the chamber by warming the sample and collecting the vapor in a calibrated volume. Similarly, other gaseous reagents (Cl_2 and NO) were introduced into the chamber via a calibrated volume. The contents of the calibrated volume were swept into the chamber with the diluent gases (oxygen or nitrogen). Ultrahigh-purity oxygen and nitrogen from Airgas Great Lakes were used as diluent gases. The loss of $C_xF_{2x+1}CHO$ was 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 time required to record a spectrum was 90 s for all experiments. A typical experiment consisted of seven irradiations for a total of 16 min blacklight irradiation. The average temperature for the experiments was 298 ± 3 K.

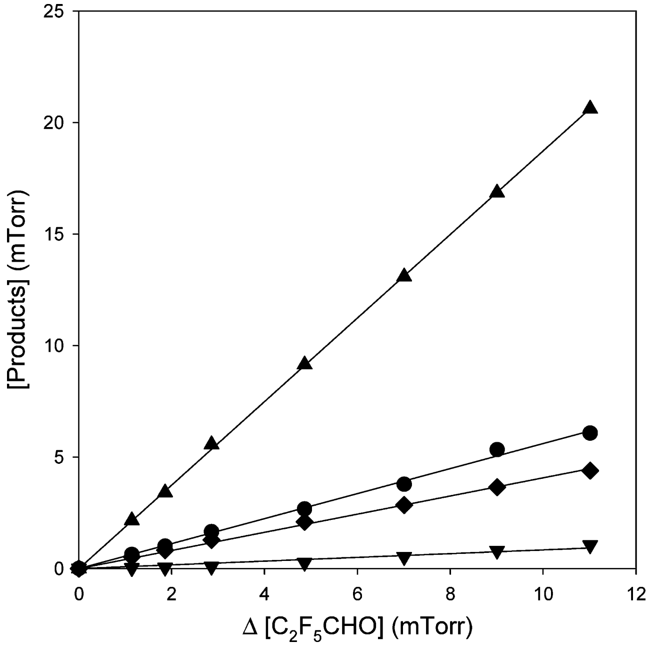

Figure 2. Yields of CO (circles), CO_2 (diamonds), $C_2F_5C(O)O_2NO_2$ (triangles down), and COF_2 (triangles up) versus loss of C_2F_5CHO following Cl-initiated oxidation in the presence of NO. The observed product yields are 56.1 ± 7.2% CO, 40.7 ± 5.0% CO_2, 187 ± 20% COF_2, and 8.3 ± 2.0% $C_2F_5C(O)O_2NO_2$.

During the Cl-initiated oxidation of $C_xF_{2x+1}CHO$, CF_3O and CF_3O_2 radicals are formed. Both CF_3O and CF_3O_2 radicals may react with CO.[25]

$$CF_3O + CO \rightarrow CF_3 + CO_2 \qquad (6)$$

$$CF_3O_2 + CO \rightarrow CF_3O + CO_2 \qquad (7)$$

In preliminary experiments the yield plots of CO were curved, suggesting that one, or both, of these reactions are important under our experimental conditions. NO reacts rapidly with CF_3O and CF_3O_2, $k_8 = (5.2 \pm 2.7) \times 10^{-11}$[26] and $k_9 = (1.68 \pm 0.26) \times 10^{-11}$[26] cm^3 $molecule^{-1}$ s^{-1}, respectively.

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \qquad (8)$$

$$CF_3O + NO \rightarrow COF_2 + FNO \qquad (9)$$

To avoid complications from CF_3O and CF_3O_2 radicals, all experiments were conducted in the presence of NO.

3. Results and Discussion

The focus of this study is the fate of the $C_xF_{2x+1}C(O)$ radical. Experiments were performed to investigate the mechanism of

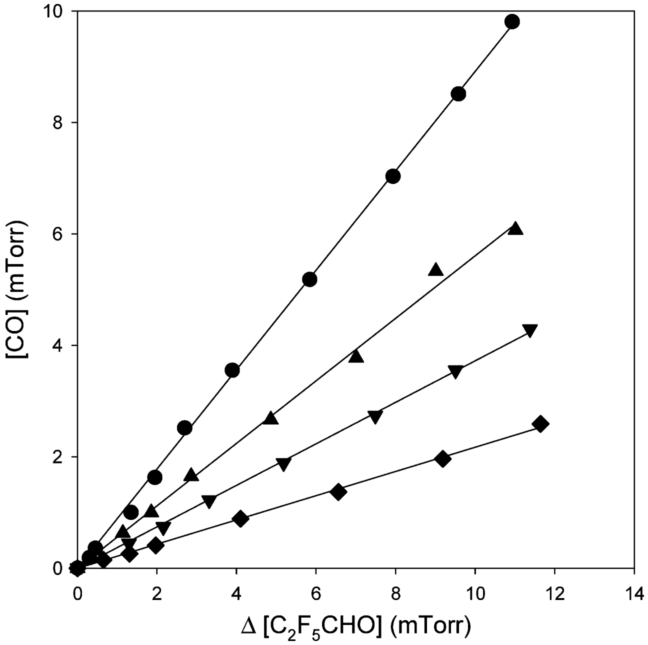

Figure 3. Plot of the observed formation of CO versus the loss of C_2F_5CHO following the irradiation of $C_2F_5CHO/Cl_2/NO/O_2$ mixtures in 700 Torr N_2. The experiments were performed with O_2 concentrations of 0 Torr (circles), 100 Torr (triangles up), 200 Torr (triangles down), and 600 Torr (diamonds).

TABLE 1: CO Yields Observed during the Cl-Initiated Oxidation of $C_xF_{2x+1}CHO$ ($x = 1, 2, 3, 4$) in the Presence of NO_X in 0−650 Torr O_2, 700 Torr Total Pressure

O_2 (Torr)	CF_3CHO	C_2F_5CHO	C_3F_7CHO	C_4F_9CHO
0	0.83 ± 0.09	0.89 ± 0.10	0.90 ± 0.10	0.97 ± 0.11
5	0.27 ± 0.03			
10	0.19 ± 0.02			
15	0.14 ± 0.02			
20	0.11 ± 0.01			
25	0.09 ± 0.01			
100		0.56 ± 0.07	0.83 ± 0.09	0.93 ± 0.11
200		0.37 ± 0.04	0.73 ± 0.08	0.81 ± 0.09
300		0.34 ± 0.04	0.65 ± 0.07	0.75 ± 0.09
400		0.28 ± 0.03	0.57 ± 0.07	0.77 ± 0.10
500		0.24 ± 0.03	0.56 ± 0.07	0.66 ± 0.08
650		0.22 ± 0.03	0.50 ± 0.05	0.68 ± 0.08

Cl-atom-initiated oxidation of $C_xF_{2x+1}CHO$ in the presence of NO_X. In the presence of NO, CO was observed as a product and CO yield plots were linear with an intercept through the origin. Mixtures consisting of 7−26 mTorr $C_xF_{2x+1}CHO$, 15−32 mTorr NO, and 100 mTorr Cl_2 in 700 Torr of O_2/N_2 diluent gas were irradiated using UV blacklamps.

Figure 1 shows spectra acquired before (panel A) and after (panel B) a 4-min irradiation of a gas mixture consisting of 14.3 mTorr C_2F_5CHO, 29.4 mTorr NO, 100 mTorr Cl_2, and 100 Torr O_2 pressurized to 700 Torr with N_2. The consumption of C_2F_5CHO was 34%. Figure 1C is the IR spectrum of the products. The spectral features of NOCl have been removed from panel C for clarity. Comparison of the IR features in panel C with the reference spectra of CO, CO_2, and COF_2 in panels D−F shows these compounds to be among the products formed. Also observed in the product spectrum were the IR spectral features of $C_2F_5C(O)O_2NO_2$ at 791, 991, 1111, 1242, 1301, 1762, and 1850 cm^{-1} showing $C_2F_5C(O)O_2NO_2$ to be a minor product.

Figure 2 shows the observed formation of products versus the loss of C_2F_5CHO following successive irradiations of the mixture described above. The lines through the data are least-squares fits (forced through zero) which give molar product yields of 8.3 ± 2.0% $C_2F_5C(O)O_2NO_2$, 40.7 ± 5.0% CO_2, 56.1 ± 7.2% CO, and 187 ± 20% COF_2. Quoted errors are two relative standard deviations from the regression analysis, together with an additional 10% error to reflect uncertainties associated with calibration of the reference spectra. The sum of the yields of $C_2F_5C(O)O_2NO_2$, CO_2, and CO is 105 ± 12%. The observed yield of COF_2, 187 ± 20%, is indistinguishable from 200% − $Y(C_2F_5C(O)O_2NO_2)$.

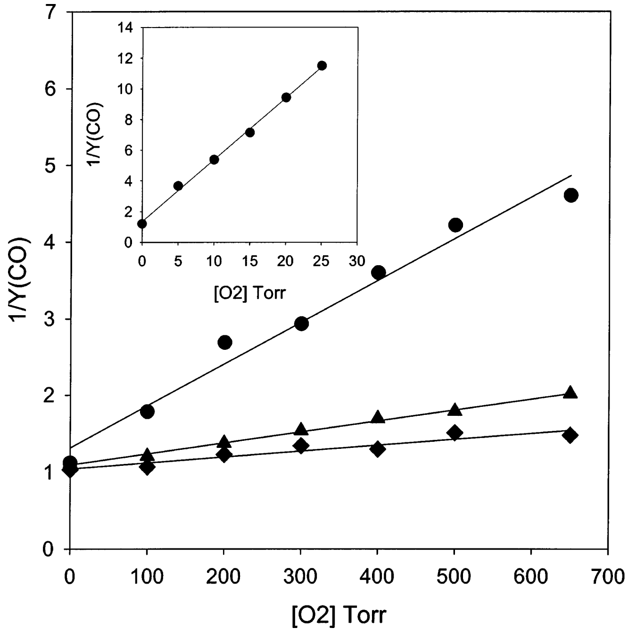

Figure 4. Plot of the reciprocal of the CO yield versus the O_2 concentration following the irradiation of $C_xF_{2x+1}CHO/Cl_2/NO/O_2$ in 700 Torr N_2 for $x = 1$ (insert), 2 (circles), 3 (triangles up), and 4 (diamonds). The lines are linear least-squares fits (see text for details).

The simplest explanation for the observed product distribution is that reaction 5 is followed by

$$C_xF_{2x+1}C(O) + O_2 + M \rightarrow C_xF_{2x+1}C(O)O_2 + M \quad (2)$$

$$C_xF_{2x+1}C(O)O_2 + NO_2 \rightarrow C_xF_{2x+1}C(O)O_2NO_2 \quad (10)$$

$$C_xF_{2x+1}C(O)O_2 + NO \rightarrow C_xF_{2x+1}C(O)O + NO_2 \quad (11)$$

$$C_xF_{2x+1}C(O)O \rightarrow C_xF_{2x+1} + CO_2 \quad (12)$$

$$C_xF_{2x+1}C(O) + M \rightarrow C_xF_{2x+1} + CO + M \quad (3)$$

$$C_xF_{2x+1} + O_2 + M \rightarrow C_xF_{2x+1}O_2 + M \quad (13)$$

$$C_xF_{2x+1}O_2 + NO \rightarrow C_xF_{2x+1}O + NO_2 \quad (14)$$

$$C_xF_{2x+1}O + M \rightarrow C_{x-1}F_{2x-1} + COF_2 + M \quad (15)$$

Repetition of reactions 13−15 results in the "unzipping" of the radical and the formation of $x - 1$ molecules of COF_2 for $C_xF_{2x+1}CHO$ ($x = 1, 2, 3, 4$). The last radical formed, CF_3, will be converted into COF_2 by reactions 16, 8, and 9.

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \quad (16)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \quad (8)$$

$$CF_3O + NO \rightarrow COF_2 + FNO \quad (9)$$

TABLE 2: Branching Ratios in Reactions of $C_xF_{2x+1}C(O)O_2$ (x = 1, 2, 3, 4) with HO_2 Radicals under Ambient Conditions (700 Torr air, 298 ± 3 K)

			$RC(O)O_2 + HO_2 \rightarrow$ Products			
RC(O)	$RC(O)O_2$ reaction 2	R + CO reaction 3	$RC(O)OOH + O_2$ reaction 19a	$RC(O)OH + O_3$ reaction 19b	$RC(O)O + OH + O_2$ reaction 19c	ref
$CH_3C(O)$	100%	0%	40 ± 16%	20 ± 8%	40 ± 16%	27
$CF_3C(O)$	98%	2%	9 ± 4%	39 ± 4%	52 ± 5%	this work
$C_2F_5C(O)$	48%	52%	<12%	50 ± 8%	50 ± 8%	this work
$C_3F_7C(O)$	19%	81%	<16%	53 ± 11%	47 ± 11%	this work
$C_4F_9C(O)$	11%	89%	<27%	73 ± 18%	27 ± 18%	this work

In the presence of NO, NO_2 is formed during the reaction sequence given above and $C_xF_{2x+1}C(O)O_2NO_2$ and CF_3ONO_2 are expected to be formed via reactions 17 and 18.

$$C_xF_{2x+1}C(O)O_2 + NO_2 + M \rightarrow C_xF_{2x+1}C(O)O_2NO_2 + M \quad (17)$$

$$CF_3O + NO_2 + M \rightarrow CF_3ONO_2 + M \quad (18)$$

In determining the fate of the $C_xF_{2x+1}C(O)$ radical in the atmosphere, it is important to know the relative importance of reactions 2 and 3. Assuming that reactions 2−18 describe the chemistry occurring following the irradiation of mixtures of $C_xF_{2x+1}CHO$, NO, O_2, and Cl_2, and assuming that CO, CO_2, and $C_xF_{2x+1}C(O)O_2NO_2$ are not lost in any process, then the sum of the molar yields of CO, CO_2, and $C_xF_{2x+1}C(O)O_2NO_2$ should be 100%. This was observed experimentally. The relative yields of CO, CO_2, and $C_xF_{2x+1}C(O)O_2NO_2$ depended on the O_2 and NO_2 partial pressures. The yield of CO increased at low O_2 concentration with a corresponding decrease in the combined yield of CO_2 and $C_xF_{2x+1}C(O)O_2NO_2$. As an example, in the reaction of C_2F_5CHO in 100 Torr O_2, the CO yield was 56 ± 7% and the combined yield of CO_2 and $C_xF_{2x+1}C(O)O_2NO_2$ was 49 ± 5%. In 650 Torr O_2, the CO yield was 22 ± 3% and the combined yield of CO_2 and $C_xF_{2x+1}C(O)O_2NO_2$ was 90 ± 10%.

Assuming that (i) CO is produced only from reaction 3, (ii) reactions 2 and 3 are the sole fate of $C_xF_{2x+1}C(O)$ radicals, and (iii) CO is not lost by any process, the expression I holds:

$$\frac{1}{Y(CO)} = 1 + \left(\frac{k_2}{k_3}\right) \times [O_2] \quad (I)$$

where Y(CO) is the molar yield of CO, k_2 and k_3 are the rate constants of reactions 2 and 3, and $[O_2]$ is the concentration of oxygen. Experiments were performed with oxygen partial pressures varied over the range 0−25 Torr for experiments with CF_3CHO and 0−650 Torr for experiments with $C_xF_{2x+1}CHO$ (x = 2, 3, 4). In all cases, nitrogen was added to give 700 Torr total pressure.

Figure 3 shows the CO yield plots for mixtures of C_2F_5CHO, Cl_2, and NO in 0, 100, 200, and 650 Torr oxygen, 700 Torr total pressure. Experiments at 300, 400, and 500 Torr oxygen have been omitted for clarity. The CO yields observed during the Cl-initiated oxidation of $C_xF_{2x+1}CHO$ (x = 1, 2, 3, 4) in the presence of NO_X in 0, 100, 200, 300, 400, 500, and 650 Torr oxygen are given in Table 1.

Figure 4 shows a plot of 1/Y(CO) versus $[O_2]$ for $C_xF_{2x+1}CHO$ (x = 1, 2, 3, 4). The experimenal data are consistent with analytical expression I. Linear least-squares analysis of the data in Figure 4, forced through a y-axis intercept of one, gives a slope, k_2/k_3, of $(1.30 \pm 0.05) \times 10^{-17}$, $(1.90 \pm 0.17) \times 10^{-19}$, $(5.04 \pm 0.40) \times 10^{-20}$, and $(2.67 \pm 0.42) \times 10^{-20}$ cm^3 molecule^{-1} for $C_xF_{2x+1}CHO$ (x = 1, 2, 3, 4), respectively. As seen in Table 1, the y-axis intercept is slightly greater than one for all compounds studied. This is probably due to oxygen impurities in the nominally oxygen-free reaction mixtures or the formation of $C_xF_{2x+1}C(O)Cl$ via reaction of $C_xF_{2x+1}C(O)$ radicals with Cl_2.

The rate constant ratio, k_2/k_3, for CF_3CHO has been determined previously[25] to be $(7.4 \pm 0.6) \times 10^{-18}$ cm^3 molecule^{-1}, which is smaller than the value determined in this work by a factor of approximately two. As part of this work, the previous work was reviewed and it was determined that the CO reference spectrum used in the previous work was calibrated incorrectly. The value determined in this work supersedes the previous value.

Solignac et al.[19] observed CO as a primary product during the Cl-initiated oxidation of $C_3F_{17}CHO$ and $C_6F_{13}CHO$. The yield of CO from C_3F_7CHO was dependent on the oxygen concentration and was determined to be 61 ± 2% in 1000 mbar of air and 85 ± 5% in 1000 mbar of nitrogen. This corresponds to a rate constant ratio $k_2/k_3 = k_{O_2}/k_{diss} = 1.25 \times 10^{-19}$ cm^3 molecule^{-1}. This value is approximately 100% greater than our value of $k_{O_2}/k_{diss} = (5.04 \pm 0.40) \times 10^{-20}$ cm^3 molecule^{-1} for C_3F_7CHO. The reason for this discrepancy is not clear, however, Solignac et al.[19] performed their experiments in the absence of NO. In the absence of NO, it is possible that CF_3O and/or CF_3O_2 reacts with CO as given in reactions 6 and 7. If CO is lost by such reactions, the reported yield will be low and the observed rate constant ratio will be too large, consistent with the discrepancy between our work and that of Solignac et al.[19]

4. Implications for Atmospheric Chemistry

The goal of the present work was to determine the fate of the $C_xF_{2x+1}C(O)$ (x = 1, 2, 3, 4) radical. The results presented here improve our understanding of the atmospheric chemistry of the $C_xF_{2x+1}C(O)$ radical and show that these radicals both decompose to give C_xF_{2x+1} and CO and react with O_2 to give $C_xF_{2x+1}C(O)O_2$ radicals. At 298 ± 3 K and 760 Torr air (160 Torr O_2), 1%, 50%, 79%, and 88% of $C_xF_{2x+1}C(O)$ radicals will decompose to C_xF_{2x+1} and CO for x = 1, 2, 3, and 4, respectively. Accordingly, 99%, 50%, 21%, and 12% of $C_xF_{2x+1}C(O)$ radicals will react with O_2 to give $C_xF_{2x+1}C(O)O_2$ radicals, for x = 1, 2, 3, and 4, respectively. In Earth's atmosphere, both temperature and pressure decrease with increasing altitude. As discussed previously,[20,21,25] the effects of reduced temperature and pressure favor reaction 2 over reaction 3. Quantification of the relative importance of reactions 2 and 3 in the atmosphere requires detailed knowledge of the temperature- and pressure-dependence of reactions 2 and 3 for $C_xF_{2x+1}C(O)$. Barnes et al.[20] have studied the effect of temperature and pressure on k_2/k_3 for $CF_3C(O)$ radicals, report an activation barrier for decomposition of 40.8 ± 9.9 kJ mol^{-1}, and estimate that the fraction of $CF_3C(O)$ radicals lost via decomposition is 1.3% at 298 K and 1000 mbar. There are no available data concerning the temperature- or pressure-dependence of the ratio k_2/k_3 for $C_xF_{2x+1}C(O)$ with $x > 1$.

In previous work,[15−18] the reaction of $C_xF_{2x+1}C(O)$ with O_2 was assumed to be the sole fate of $C_xF_{2x+1}C(O)$ radicals in 700 Torr air at 296 K. This was justified on the basis of previous results for $CF_3C(O)$.[25] Results from the present work show the importance of the decomposition channel and allow a refinement of branching ratios given previously for the reaction of $C_xF_{2x+1}C(O)O_2$ with HO_2. The reaction was reported to proceed via three pathways:

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)OOH + O_2 \quad (19a)$$

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)OH + O_3 \quad (19b)$$

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)O + O_2 + OH \quad (19c)$$

The previous studies of $C_xF_{2x+1}C(O)O_2$ ($x = 1, 2, 3, 4$) with HO_2 were conducted at 296 ± 2 K and 700 Torr air diluent. Using the results from the present work, the fraction of $C_xF_{2x+1}C(O)$ radicals that react with O_2 to form $C_xF_{2x+1}C(O)O_2$ radicals in 700 Torr air (147 Torr O_2) is calculated to be 98%, 48%, 19%, and 11% for $x = 1, 2, 3, 4$, respectively. In establishing the branching ratio for reaction 19, the product yields need to be adjusted to account for the fraction of radicals that decompose. For example, previously the overall yield of $C_2F_5C(O)OH$ from the Cl-initiated oxidation of C_2F_5CHO in the presence of HO_2 was determined to be 24%. Since the yield of $C_2F_5C(O)O_2$ radicals is 48%, the adjusted yield of $C_2F_5C(O)OH$ from the reaction of $C_2F_5C(O)O_2$ with HO_2 is 0.24/0.48 = 50%. No peracid, $C_2F_5C(O)OOH$, was observed, and an upper limit of 6% was established. The adjusted upper limit of peracid yield from the reaction of $C_2F_5C(O)O_2$ with HO_2 is 0.06/0.48 = 12%. The overall yield of $C_2F_5C(O)O$ radicals, 76%, was calculated from the formation of the decomposition products, COF_2 and CF_3OH. However, COF_2 and CF_3OH are not unique to the oxidation channel since they are also formed from the $C_2F_5O_2$ radicals generated in the decomposition channel. It seems reasonable to assume that reaction 19c accounts for the balance of the carbon. The simplest explanation of the observed products is that reaction 19 proceeds <12% via reaction 19a, 50% via channel 19b, and 50% via channel 19c. Similar adjustments were made to the branching ratios for $C_xF_{2x+1}C(O)O_2$ ($x = 1, 3, 4$), and the results are shown in Table 2, which supersedes Table 1 in ref 18.

In the Introduction, two gas-phase chemical mechanisms by which $C_xF_{2x+1}CHO$ is converted into perfluorocarboxylic acids are described. The first mechanism is oxidation to $C_xF_{2x+1}C(O)O_2$ radicals followed by reaction with HO_2 radicals to give $C_xF_{2x+1}C(O)OH$. The second mechanism involves oxidation to $C_xF_{2x+1}O_2$ radicals and their reaction with CH_3O_2 to give $C_xF_{2x+1}OH$.[14] The results from Solignac et al.[19] and the present work show that in the atmosphere a significant fraction of $C_xF_{2x+1}C(O)$ radicals will decompose, thereby limiting the formation of $C_xF_{2x+1}C(O)O_2$ radicals.

In previous work from our laboratories we assumed (incorrectly) that reaction with O_2 was the sole atmospheric fate of $C_xF_{2x+1}C(O)$ radicals.[15-18] Relative to our previous understanding (as incorporated in the global modeling work), recognition of the decomposition of $C_xF_{2x+1}C(O)$ radicals via reaction 3 has two effects. First, it *decreases* the yield of $C_xF_{2x+1}C(O)O_2$ radicals formed during the atmospheric degradation of fluorotelomer alcohols by a factor of $(k_2[O_2] + k_3)/k_2[O_2]$. Second, it *increases* the perfluorocarboxylic acid yield in the reaction of $C_xF_{2x+1}C(O)O_2$ radicals with HO_2 by a factor of $(k_2[O_2] + k_3)/k_2[O_2]$. The two effects offset each other, and the PFCA yield from the first mechanism is unchanged at 298 K. In the mechanism used in our previous global modeling work, the reaction of $C_8F_{17}C(O)H$ with OH radicals was assumed to lead ultimately either to the formation of $C_8F_{17}C(O)OH$ (via reaction 19b) or $C_8F_{17}O_2$ radicals. In the mechanism used in the global modeling work, the majority (>90%) of radicals formed in the OH + $C_8F_{17}CHO$ reaction are converted into $C_8F_{17}O_2$ radicals. Recognition of the decomposition of $C_xF_{2x+1}C(O)$ radicals via reaction 3 does not alter the yield of $C_8F_{17}O_2$ radicals (although it does alter the mechanism leading to their formation) and hence PFCAs via the second mechanism. Accounting for decomposition of $C_xF_{2x+1}C(O)$ radicals via reaction 3 is not expected to lead to a material change in the predicted PFCA yield from the atmospheric oxidation of fluorotelomer alcohols such as $C_8F_{17}CH_2CH_2OH$. Finally, we note that information concerning the temperature- and pressure-dependence of k_2/k_3 for large $C_xF_{2x+1}C(O)$ radicals ($x > 4$) is needed for a more accurate description of their chemistry in global atmospheric models.

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