Atmospheric chemistry of C_2F_5CHO:
mechanism of the $C_2F_5C(O)O_2 + HO_2$ reaction

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Abstract

Smog chamber/FTIR techniques were used to study the gas-phase reaction of $C_2F_5C(O)O_2$ with HO_2 radicals in 100–700 Torr of air, or O_2, diluent at 296 K. The reaction proceeds by two pathways leading to formation of $C_2F_5C(O)OH$ and O_3 in a yield of $24 \pm 4\%$ and $C_2F_5C(O)O$ radicals, OH radicals and O_2 in a yield of $76 \pm 4\%$. The gas phase reaction of $C_nF_{2n+1}C(O)O_2$ with HO_2 radicals offers a potential explanation for at least part of the observed environmental burden of fluorinated carboxylic acids, $C_nF_{2n+1}C(O)OH$. As part of this work an upper limit for the rate constant of reaction of Cl atoms with $C_2F_5C(O)OH$ at 296 K was determined; $k(Cl + C_2F_5C(O)OH) < 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.
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1. Introduction

Long-chain perfluorinated carboxylic acids (PFCAs, $C_nF_{2n+1}C(O)OH$, where $n = 6$–12) have been observed recently in fish [1] and mammals [2] in a variety of locations around the world. Perfluorinated acids have no known significant biotic or abiotic degradation loss mechanisms in the environment, and are bioaccumulative when the perfluorinated chain reaches a length of six or

more carbon atoms [3,4]. The health effects associated with long-term exposure to perfluorinated acids are the subject of a present risk assessment [5]. In animal studies and in vitro tests, perfluorinated acids are potent peroxisome proliferators [6], inhibitors of gap-junction intercellular communication [7], and tumor promoters [8].

PFCAs are not generally used directly in consumer or industrial materials, other than in aqueous film forming foams or as polymerization aids in fluoropolymer manufacture [9]. The PFCAs observed in the environment are presumably the degradation products of precursor chemicals. The identity of the precursors and mechanism by which

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they are converted into PFCAs are unknown at the present time.

Fluorotelomer alcohols, $C_nF_{2n+1}CH_2CH_2OH$, are used in a variety of industrial products (paints, coatings, polymers, adhesives, waxes, polishes, electronic materials, and caulks [10]). Global production has been estimated at 5×10^6 kg year^{-1}. As a result of the telomerization manufacturing process the fluoroalkyl chains tend to have even numbered carbon chain lengths (e.g. C_4, C_6, ..., C_{16}). Fluorotelomer alcohols (FTOHs) are named according to the number of fluorinated carbons within the chain as compared with the number of hydrogenated carbon atoms, e.g. 4:2 FTOH = $C_4F_9CH_2CH_2OH$. 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH have been observed in the atmosphere (at pg m^{-3} concentrations [11,12]) and it has been shown experimentally that fluorinated aldehydes are formed during the atmospheric oxidation of FTOHs. For example, C_4F_9CHO, $C_6F_{11}CHO$, and $C_8F_{17}CHO$ have been identified as products of the simulated atmospheric oxidation of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH [13].

It is well established that the atmospheric oxidation of acetaldehyde, CH_3CHO, proceeds via the formation of acetyl peroxy radicals, $CH_3C(O)O_2$. Furthermore, it is known that $CH_3C(O)O_2$ react with HO_2 radicals in the atmosphere via two channels:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \tag{1a}$$

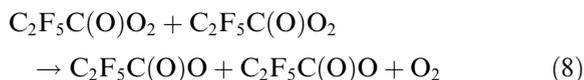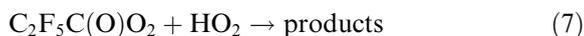$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3 \tag{1b}$$
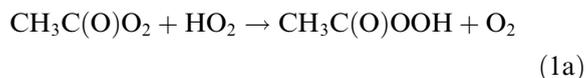
On the basis of a review of the literature data [14–18], Tyndall et al. [19] recommend $k_{1a}/k_{1b} = 4$ in one atmosphere of air at 298 K (i.e., $k_{1b}/(k_{1a} + k_{1b}) = 20\%$). It is possible that a reaction channel analogous to (1b) is important in the atmospheric chemistry of fluorinated acyl peroxy radicals of the general formula $C_nF_{2n+1}C(O)O_2$. If so, this reaction may be a source of the perfluorocarboxylic acids observed in the environment. Unfortunately, there are no available kinetic or mechanistic data with which to make a determination of the likely importance of this source. To improve this situation we have used smog chamber FTIR techniques to study the mechanism of the reaction of

$C_2F_5C(O)O_2$ with HO_2. Results are reported herein and discussed with respect to the atmospheric chemistry and environmental impact of fluorinated organic compounds. Chemical intuition, combined with our recent experience with long-chain fluorinated alcohols [20] and acids [21] suggests that C_2F_5CHO will serve as a useful model with which to understand the degradation mechanism of longer chain perfluoroaldehydes.

2. Experimental

The apparatus and experimental techniques used in this work are described in detail elsewhere [22]. Experiments were performed in a 140-liter 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. $C_2F_5C(O)O_2$ and HO_2 radicals were generated by the UV irradiation of $C_2F_5CHO/H_2/Cl_2$ mixtures in 100–700 Torr of air, or O_2, diluent at 296 ± 2 K (M represents a third body, N_2 or O_2).

$$Cl_2 + h\nu \rightarrow 2Cl \tag{2}$$

$$Cl + C_2F_5CHO \rightarrow C_2F_5CO + HCl \tag{3}$$

$$C_2F_5CO + O_2 + M \rightarrow C_2F_5C(O)O_2 + M \tag{4}$$

$$Cl + H_2 \rightarrow H + HCl \tag{5}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{6}$$

$$C_2F_5C(O)O_2 + HO_2 \rightarrow products \tag{7}$$

$$C_2F_5C(O)O_2 + C_2F_5C(O)O_2$$
$$\rightarrow C_2F_5C(O)O + C_2F_5C(O)O + O_2 \tag{8}$$

Initial concentrations of the gas mixtures used were 2.6–22.5 mTorr of C_2F_5CHO, 88–440 mTorr of Cl_2, and 223–4511 mTorr of H_2 in 700 or 100 Torr of air or oxygen diluent (ultra high purity). Reactions (7) and (8) are competing loss mechanisms for $C_2F_5C(O)O_2$ in the system. To study the mechanism of reaction (7) a series of experiments was performed in which the initial concentration ratio $[H_2]_0/[C_2F_5CHO]_0$ was varied from 0 to 1545. The

rate constant ratio k_3/k_5 is $1.97 \times 10^{-12}/1.73 \times 10^{-14} = 114$ [23,28]. Thus, the initial rate of production of HO_2 radicals was 0–13.6 times that of $C_2F_5C(O)O_2$ radicals. As the $[H_2]_0/[C_2F_5CHO]_0$ ratio increases, more HO_2 radicals are generated in the system for a given level of $C_2F_5C(O)O_2$ and the relative importance of reaction (7) as a loss mechanism for $C_2F_5C(O)O_2$ increases. The increased importance of reaction (7) should be manifested by a change in the products observed in the system. For sufficiently high values of $[H_2]_0/[C_2F_5CHO]_0$ essentially all of the $C_2F_5C(O)O_2$ radicals should be lost via reaction (7). At this point, further increases in $[H_2]_0/[C_2F_5CHO]_0$ will have no discernable effect on the observed products which can then be ascribed to reaction (7). This general approach has been used in previous studies of the reactions of HO_2 radicals with CH_2FO_2 [24], CH_2ClO_2 [25], $CHCl_2O_2$ [26], CCl_3O_2 [26], $CH_3OCH_2O_2$ [27], and $CH_3C(O)O_2$ [18].

Reactant and product concentrations were monitored using in situ Fourier transform infrared 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. Reference spectra were acquired by expanding calibrated volumes of reference materials into the chamber. The vapor above liquid $C_2F_5C(O)OH$ contains monomer and dimer. A value of $K_{eq} = [\text{Dimer}]/[\text{Monomer}]^2 = 0.30 \pm 0.03$ Torr^{-1} [21] was used to correct for $C_2F_5C(O)OH$ dimer (5–26% partial pressure) in the calibrated volumes. Analysis of the IR spectra was achieved through a process of spectral stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum.

C_2F_5CHO was synthesized as described elsewhere [28] and purified by vacuum distillation. All other reactants were obtained from commercial sources at purities >99%. Ultrahigh purity air (THC < 0.1 ppm) and O_2 (>99.994%) diluent gases were used as received. In smog chamber experiments unwanted loss of reactants and products via photolysis and heterogeneous reactions has to be considered. Control experiments were performed in which product mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable

(<2%) loss of reactants or products. Samples of C_2F_5CHO and $C_2F_5C(O)OH$ were subjected to UV irradiation in 700 Torr of air diluent for 15 min without any observable loss (<1%) suggesting that photolysis of C_2F_5CHO and $C_2F_5C(O)OH$ is not a significant complication in the present work.

3. Results

Prior to the study of the mechanism of reaction (7) an experiment was performed to investigate the rate of reaction of Cl atoms with $C_2F_5C(O)OH$ using the relative rate technique. A mixture containing 3 mTorr $C_2F_5C(O)OH$, 5 mTorr CF_2ClH and 1.1 Torr of Cl_2 in 700 Torr of N_2 was introduced into the chamber. Irradiation of the gas mixture for 3 min led to 89% consumption of CF_2ClH but no discernable loss (<1%) of $C_2F_5C(O)OH$. Using $k(\text{Cl} + CF_2ClH) = 1.7 \times 10^{-15}$ [23] we derive an upper limit of $k(\text{Cl} + C_2F_5C(O)OH) < 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. This result can be compared to our previous determination of $k(\text{Cl} + CF_3C(O)OH) < 1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} [29]. There is little, or no, reaction of Cl atoms with perfluorocarboxylic acids under ambient conditions.

Fig. 1 shows typical spectra acquired before (A) and after (B) a 35 s irradiation of a mixture of 18.8 mTorr of C_2F_5CHO, 2.84 Torr of H_2, and 218 mTorr of Cl_2 in 700 Torr of air diluent. The loss of C_2F_5CHO was 8.5 mTorr. Comparison with reference spectra of $C_2F_5C(O)OH$, COF_2, and CF_3OH shown in panels C, D and E indicates the formation of these species. The sharp peaks of $C_2F_5C(O)OH$, COF_2, and CF_3OH are located at 3577, 1944, and 3664 cm^{-1}, respectively. Features attributable to the peracid $C_2F_5C(O)OOH$ were sought but not found. On the basis of the strength of the carbonyl absorption feature of peracetic acid, $CH_3C(O)OOH$, we estimate an upper limit of 6% for the formation of $C_2F_5C(O)OOH$.

Fig. 2 shows a plot of the observed formation of $C_2F_5C(O)OH$ versus the loss of C_2F_5CHO for a series of experiments with $[H_2]_0/[C_2F_5CHO]_0$ ranging from 18.3 to 1034.9 in 100–700 Torr of air, or oxygen, diluent. The linearity of the plots in Fig. 2 suggest that loss of $C_2F_5C(O)OH$ is not
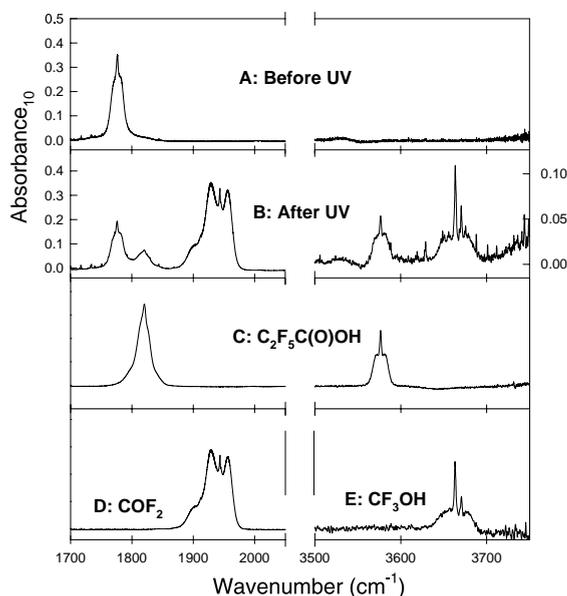
Fig. 1. IR spectra obtained before (A) and after (B) 55 s of irradiation of a mixture of 18.8 mTorr $C_2F_5C(O)H$, 218 mTorr Cl_2 and 2.8 Torr H_2 in 700 Torr of air. The consumption of $C_2F_5C(O)H$ was 63%. Panels C, D and E are reference spectra of $C_2F_5C(O)OH$, COF_2, and CF_3OH, respectively.
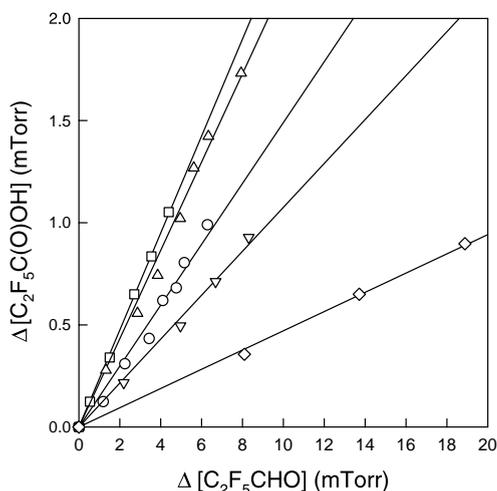

Fig. 2. Formation of C_2F_5COOH versus loss of C_2F_5CHO for experiments employing various $[H_2]_0/[C_2F_5CHO]_0$ ratios: 18.3 (diamonds, 700 Torr O_2), 89.7 (inverted triangles, 700 Torr air), 121.5 (circles, 700 Torr air), 234.0 (triangles, 100 Torr air), and 1034.9 (squares, 700 Torr air).

significant during these experiments. This is consistent with expectations given the the absence of photolytic or heterogeneous losses of

$C_2F_5C(O)OH$ and its low reactivity towards Cl atoms. The lines through the data in Fig. 2 are linear fits (unweighted, forced through origin) to the data which give molar yields of $C_2F_5C(O)OH$ in the various experiments.

The observed yields of $C_2F_5C(O)OH$ and COF_2 are plotted versus $[H_2]_0/[C_2F_5CHO]_0$ in Fig. 3. CF_3OH was measured simultaneously with COF_2 and its yield followed the same pattern as that of COF_2. As seen from a comparison of the open, gray, and filled symbols in Fig. 3 there was no discernable effect of total pressure over the range 100–700 Torr or the use of air, or O_2, diluent on the product yields. For experiments conducted in the absence of H_2 there was evidence in the product spectra for formation of the trioxides $CF_3O_3CF_3$ and $C_2F_5O_3C_2F_5$ formed by addition of CF_3O radicals to CF_3O_2 and $C_2F_5O_2$ radicals. In the presence of H_2 there was no evidence for the formation of trioxides in the system and it seems reasonable to assume that the fate of CF_3O radicals is reaction with H_2 to give CF_3OH.

As seen from Fig. 3 the yield of $C_2F_5C(O)OH$ increases as the concentration ratio $[H_2]_0/[C_2F_5CHO]_0$ is increased from 0 to 600, presumably reflecting the increased importance of reaction (1a) as a loss of $C_2F_5C(O)O_2$ radicals.

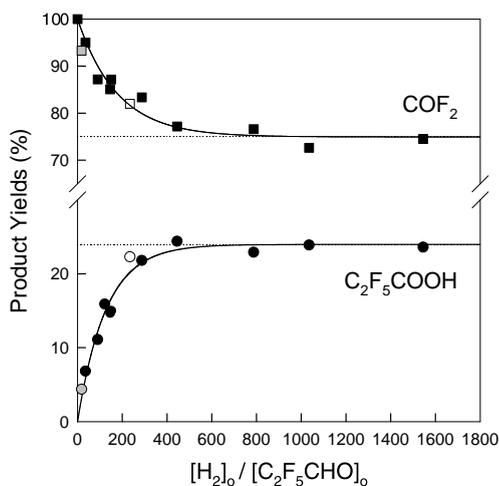Fig. 3. Yield of C_2F_5COOH following Cl atom initiated oxidation of C_2F_5CHO in the presence of HO_2 radicals versus $[H_2]_0/[C_2F_5CHO]_0$ in 700 Torr of air (filled), 700 Torr of O_2 (gray), and 100 Torr of air (open) diluent.

Concurrently, the yield of COF_2 decreases. For concentration ratios greater than 600, there is no observable dependence of product yields on $[H_2]_0/[C_2F_5CHO]_0$ suggesting that, under these conditions, essentially all the $C_2F_5C(O)O_2$ radicals are consumed by reaction with HO_2 radicals. Averaging all the product data obtained using $[H_2]_0/[C_2F_5CHO]_0$ of 600 or more, gives the following product yields; $C_2F_5C(O)OH$, $24 \pm 4\%$; COF_2, $75 \pm 5\%$; and CF_3OH $70 \pm 5\%$. Quoted errors are two standard deviations from the linear least squares regressions. Together, C_2F_5COOH, COF_2, and CF_3OH account for $97 \pm 6\%$ of the loss of $C_2F_5C(O)O_2$.

Loss of C_2F_5CHO via reaction with HO_2 radicals is a potential complication in the present work. It is known that HO_2 radicals add to HCHO and CH_3CHO to give an α-hydroxy peroxy radical [18]. In the case of C_2F_5CHO: the addition of HO_2 would give $C_2F_5CH(OH)O_2$ radicals.

$$HO_2 + C_2F_5CHO \leftrightarrow C_2F_5CH(OH)O_2 \qquad (9)$$
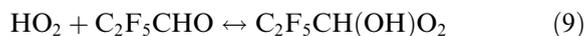
The α-hydroxy peroxy can then either decompose to reform the aldehyde and HO_2 radical, or react with HO_2 or other peroxy rad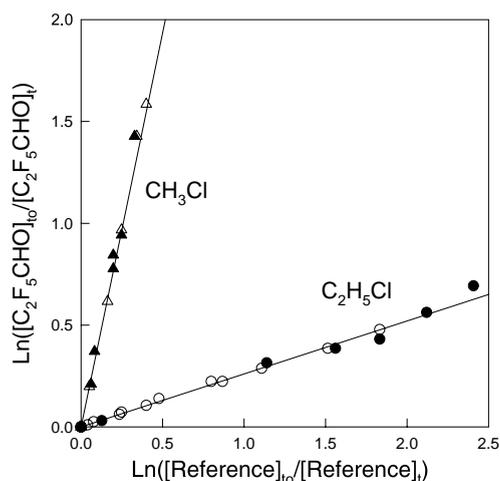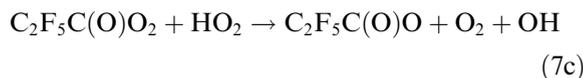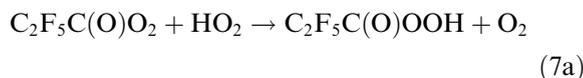icals in the system. To test for loss of C_2F_5CHO via re-action (9) experiments were performed using the UV irradiation of $C_2F_5CHO/CH_3Cl/Cl_2/H_2$ and $C_2F_5CHO/C_2H_5Cl/Cl_2/H_2$ in air diluent and the loss of C_2F_5CHO was measured relative to CH_3Cl and C_2H_5Cl. The results are compared to previous results obtained in relative rate experiments conducted in N_2 diluent in the absence of H_2 in Fig. 4. As seen from Fig. 4 the rate of loss of C_2F_5CHO relative to those of the reference compounds (CH_3Cl and C_2H_5Cl) in the presence of substantial concentrations of H_2 ($[H_2]_0/[C_2F_5CHO]_0 = 600$) was indistinguishable from that in N_2 diluent in the absence of H_2. There is no observable effect of the presence of HO_2 radicals on the rate of loss of C_2F_5CHO in the system. We conclude that reaction of C_2F_5CHO with HO_2 radicals is not a significant complication in the present work.

4. Discussion

It is expected that the reaction of HO_2 with $C_2F_5C(O)O_2$ radicals proceeds via the formation of a short lived tetraoxide intermediate. As illustrated in Fig. 5, the tetraoxide can decompose via cyclic transition states to give either the peracid and O_2, or $C_2F_5C(O)OH$ and O_3. Decomposition can also occur via $C_2F_5C(O)O–OOOH$ or $C_2F_5C(O)OOO–OH$ bond scission to give $C_2F_5C(O)O$ radicals, O_2, and OH.

$$C_2F_5C(O)O_2 + HO_2 \rightarrow C_2F_5C(O)OOH + O_2$$
$$(7a)$$

$$C_2F_5C(O)O_2 + HO_2 \rightarrow C_2F_5C(O)OH + O_3 \quad (7b)$$

$$C_2F_5C(O)O_2 + HO_2 \rightarrow C_2F_5C(O)O + O_2 + OH$$
$$(7c)$$

The observed formation of $C_2F_5C(O)OH$ in a molar yield of 24% shows that channel (7b) plays a role in the reaction. Evidence for the formation of ozone (the co-product of $C_2F_5C(O)OH$ in channel (7b)) was sought in the IR spectra, but not found. The absence of observable amounts of O_3 can be rationalized by the fact that Cl atoms react with O_3 at a rate which is 1.2×10^{-11} [23]$/2.0 \times 10^{-12}$ [28] $= 6$ times faster than the reaction with C_2F_5CHO.

Fig. 4. Loss of C_2F_5CHO versus the reference compounds CH_3Cl (triangles) and C_2H_5Cl (circles) following UV irradiation of either $C_2F_5CHO/Cl_2/reference/N_2$ (open symbols) or $C_2F_5CHO/Cl_2/reference/H_2/air$ mixtures (filled symbols). See text for details.
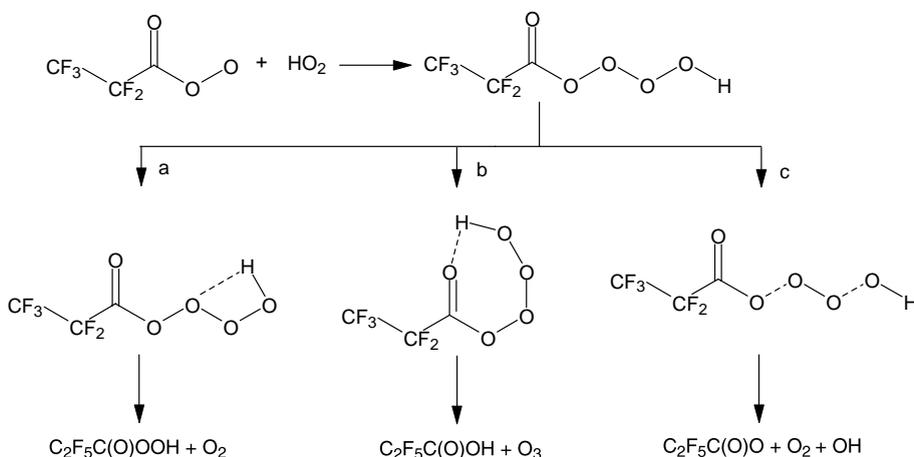
Fig. 5. Mechanistic pathways for the $C_2F_5C(O)O_2 + HO_2$ reaction.
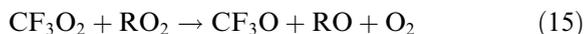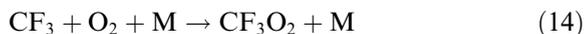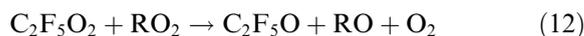
For the initial concentrations (6 mTorr for experiments with $[H_2]_0/[C_2F_5CHO]_0 > 600$) and consumptions of C_2F_5CHO employed in the present work (10–85%) loss of O_3 via reaction with Cl atoms will keep the concentration of this product below the detection limit (0.5 mTorr).

It is interesting to note that while peracetic acid ($CH_3C(O)OOH$) is a major product (approximately 80% yield) in the reaction of $CH_3C(O)O_2$ with HO_2 [19], there was no evidence for the formation of the analogous peracid in the reaction of $C_2F_5C(O)O_2$ with HO_2 radicals. Peracetic acid is not subject to heterogeneous or photolytic loss in the chamber and reacts slowly with Cl atoms. We expect $C_2F_5C(O)OOH$ to be similarly unreactive. If $C_2F_5C(O)OOH$ was formed in the chamber we would expect to observe it. From the absence of any IR features attributable to $C_2F_5C(O)OOH$ product and from the fact that we can account for 100% of the loss of C_2F_5CHO by other products we conclude that channel (7a) is of minor importance (<10%).

$C_2F_5C(O)O$ radicals formed in channel (7c) are expected to decompose and initiate a series of reactions giving COF_2 and CF_3OH.

$$C_2F_5C(O)O \rightarrow C_2F_5 + CO_2 \qquad (10)$$

$$C_2F_5 + O_2 \rightarrow C_2F_5O_2 \qquad (11)$$

$$C_2F_5O_2 + RO_2 \rightarrow C_2F_5O + RO + O_2 \qquad (12)$$

$$C_2F_5O + M \rightarrow CF_3 + COF_2 + M \qquad (13)$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \qquad (14)$$

$$CF_3O_2 + RO_2 \rightarrow CF_3O + RO + O_2 \qquad (15)$$

$$CF_3O + H_2 \rightarrow CF_3OH + H \qquad (16)$$
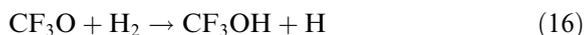
The observation of COF_2 and CF_3OH in yields which are indistinguishable from each other and which account for the balance of reaction products provides a strong indication that channel (7c) accounts for the balance of reaction not accounted for by channel (7b). The simplest explanation of the observed products is that reaction (7) proceeds $24 \pm 4\%$ via channel (7b) and $76 \pm 4\%$ via channel (7c).

It is interesting that channel (7a) does not play any discernable role in the reaction. Hydroperoxides are the dominant, if not exclusive, products of reaction of non-substituted alkyl peroxy radicals (e.g., CH_3O_2, $C_2H_5O_2$, $C_6H_{11}O_2$) with HO_2. For substituted alkyl peroxy radicals (e.g., CH_2FO_2, $CH_3OCH_2O_2$) [24,27] additional reaction channels become important. Reaction of CCl_3O_2 with HO_2 radicals proceeds exclusively via a channel leading to $CCl_3O + O_2 + OH$ [26]. The behavior of reaction (7) follows the broad pattern of other reactions of peroxy radicals with HO_2 radicals. Computational studies are needed to elucidate the factors responsible for the changes in reaction mechanisms of the different peroxy radicals.

5. Implications for atmospheric chemistry

The goal of the present work was to investigate the possibility that reaction of $C_nF_{2n+1}C(O)O_2$ with HO_2 radicals is an atmospheric source of perfluorocarboxylic acids ($C_nF_{2n+1}C(O)OH$). We show here that in 100–700 Torr of air diluent at 296 K the reaction of $C_2F_5C(O)O_2$ with HO_2 radicals gives $C_2F_5C(O)OH$ in a yield of $24 \pm 4\%$. Chemical intuition and the available data for long-chain fluorinated alcohols [20] and acids [21] suggest that $C_2F_5C(O)O_2$ is a good model with which to understand the atmospheric chemistry of larger $C_nF_{2n+1}C(O)O_2$ radicals. It seems likely that the reaction of $C_nF_{2n+1}C(O)O_2$ with HO_2 radicals will give $C_nF_{2n+1}C(O)OH$ in a yield which is comparable to that measured in the present work for $C_2F_5C(O)O_2$.

Translation of the results from the present work into an estimation of the fraction of fluorinated aldehydes in the atmosphere which are converted into fluorinated acids is complicated by three factors. First, photolysis and reaction with OH radicals are competing atmospheric fates of $C_nF_{2n+1}CHO$. Reaction with OH leads to the formation of $C_nF_{2n+1}C(O)O_2$ radicals in 100% yield. The rate and products of photolysis of $C_nF_{2n+1}CHO$ are unclear and so it is difficult to establish what fraction of $C_nF_{2n+1}CHO$ is converted into $C_nF_{2n+1}C(O)O_2$. Second, reaction with NO and HO_2 radicals are competing atmospheric fates for $C_nF_{2n+1}C(O)O_2$ radicals. Oxidation of C_2F_5CHO in the presence of excess NO *does not* lead to the formation of $C_2F_5C(O)OH$ [28]. In the absence of kinetic data for reactions with NO and HO_2 it is difficult to estimate the fraction of $C_nF_{2n+1}C(O)O_2$ which react with HO_2 radicals. Third, mechanistic data for reaction (7) are needed at temperatures in the atmospherically relevant range 220–300 K. In the analogous reaction of $CH_3C(O)O_2$ radicals the channel giving acid increases from 25% to 50% of the overall reaction over the temperature range 298–220 K. Decreasing temperature increases the tetraoxide lifetime which provides greater opportunity for the complex molecular rearrangement of the tetraoxide intermediate inherent in channel (7b). While it seems likely that channel (7b) will play a greater role in the overall reaction at lower temperatures this needs to be investigated experimentally.

In conclusion, the gas phase reaction of $C_nF_{2n+1}C(O)O_2$ with HO_2 radicals offers a qualitative explanation for the presence of fluorinated carboxylic acids, $C_nF_{2n+1}C(O)OH$, observed in the environment. Further work is required to quantify the significance of this source of $C_nF_{2n+1}C(O)OH$.

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