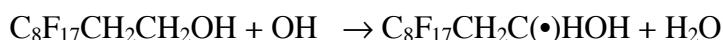


Supplementary Material

From the available kinetic and mechanistic data for 8:2 FTOH and analogous compounds the atmospheric oxidation mechanism for 8:2 FTOH shown in Table 1 was constructed. For convenience, the mechanism can be broken down into four pieces: oxidation of $C_8F_{17}CH_2CH_2OH$, $C_8F_{17}CH_2CHO$, $C_8F_{17}CHO$, and fate of $C_8F_{17}O_2$ radicals. Wet and dry deposition rates used in the model are discussed in section 2.1.5.

2.1.1 Atmospheric oxidation of $C_8F_{17}CH_2CH_2OH$

The atmospheric degradation of $C_8F_{17}CH_2CH_2OH$ is initiated by reaction with OH radicals. Measurements at ambient temperature indicate this reaction proceeds with a rate constant of $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1,2). By analogy with reactions of OH with other fluorinated organic compounds it seems likely that the temperature dependence of reaction (1) can be described using an exponential term in the Arrhenius expression of $E_a/R = 1000$ (3). Hence, we arrive at an estimate of $k(\text{OH} + C_8F_{17}CH_2CH_2OH) = 3.2 \times 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

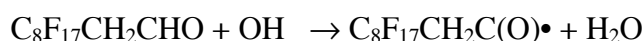


As indicated above, the reaction of OH radicals with 8:2 FTOH proceeds via attack on the CH_2 group α to the $-OH$ group. The resulting α -hydroxy alkyl radical reacts with O_2 to give the aldehyde $C_8F_{17}CH_2CHO$.

2.1.2 Atmospheric oxidation of $C_8F_{17}CH_2CHO$

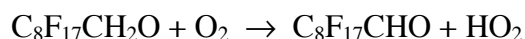
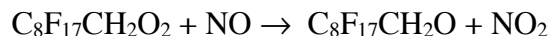
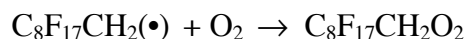
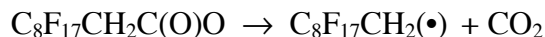
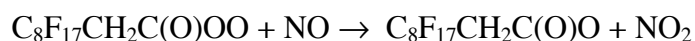
Photolysis and reaction with OH radicals are potential competing loss mechanisms for $C_8F_{17}CH_2CHO$. Unfortunately, there are no data concerning the rates of these processes. By analogy to the existing data for CF_3CH_2CHO (4,5), it is likely that reaction with OH radicals dominates the atmospheric loss of $C_8F_{17}CH_2CHO$. For

simplicity, and in the absence of evidence to the contrary, we will assume that (i) reaction with OH is the sole atmospheric loss of C₈F₁₇CH₂CHO and (ii) this reaction proceeds at the same rate as OH + CF₃CH₂CHO. From the measurements of Sellevåg et al. (5) at 298 K an average value of $k_2 = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at ambient temperature can be derived. Assuming an exponential factor of $E_a/R = 1000$ we arrive at $k(\text{OH} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}) = 1.0 \times 10^{-10} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



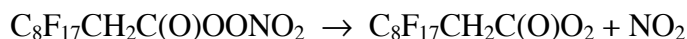
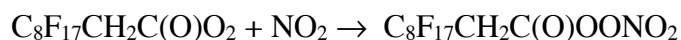
Based upon the behavior of CH₃C(O) and CF₃C(O) radicals we assume that the atmospheric fate of C₈F₁₇CH₂C(O) radicals is addition of O₂ to give an acyl peroxy radical, C₈F₁₇CH₂C(O)O₂. It seems reasonable to assume that the C₈F₁₇CH₂C(O)O₂ radical will react in the atmosphere with NO, NO₂, and HO₂ with similar rates and mechanisms as the well understood reactions involving CH₃C(O)O₂ radicals (6).

Proceeding on this assumption, reaction with NO will proceed with a rate constant of $8.1 \times 10^{-12} \exp(270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and give C₈F₁₇CH₂(•) radicals which will add O₂ to give the peroxy radical which in turn will be converted into the perfluoroaldehyde, C₈F₁₇CHO:

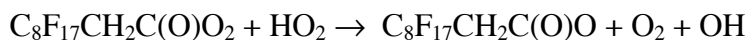
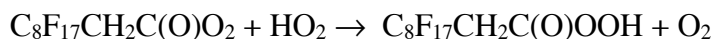
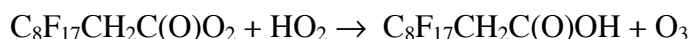


Reaction of the C₈F₁₇CH₂C(O)OO radical with NO₂ will proceed with a rate constant of $1.1 \times 10^{-11} (T/298)^{-1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to give the peroxyacetyl nitrate

$C_8F_{17}CH_2C(O)OONO_2$ which will slowly (within a few hours at ambient temperature, and few days at lower temperatures) decompose to reform the reactants:



Reaction of $C_8F_{17}CH_2C(O)O_2$ with HO_2 will have a rate constant of $4.3 \times 10^{-13} \exp(1040/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and give the acid ($C_8F_{17}CH_2C(O)OH$), peracid ($C_8F_{17}CH_2C(O)OOH$), and $C_8F_{17}CH_2C(O)O + O_2 + OH$ as products:



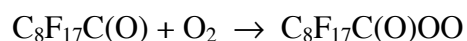
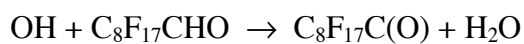
The acid ($C_8F_{17}CH_2C(O)OH$) and peracid ($C_8F_{17}CH_2C(O)OOH$) are likely to be relatively unreactive with respect to further gas-phase chemistry and will probably be lost from the atmosphere via wet and/or dry deposition. We will not consider the fate of these products further. As described above, $C_8F_{17}CH_2C(O)O$ radicals are expected to be converted into $C_8F_{17}CHO$. Based upon the latest information for the $CH_3C(O)O_2 + HO_2$ reaction (7), we assume that the yield of $C_8F_{17}CHO$ is 40% with the balance of reaction giving the acid and peracid. We assume that this branching is independent of temperature.

2.1.3 Atmospheric oxidation of $C_8F_{17}CHO$

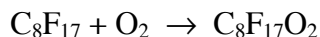
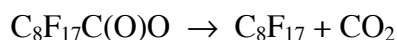
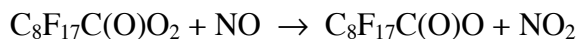
Oxidation of $C_8F_{17}CHO$ is initiated by both reaction with OH radicals and photolysis. Sellevåg et al. (5) have established an upper limit of $\Phi \leq 0.02$ for the photodissociation quantum yield of CF_3CHO in sunlight. We assume $\Phi = 0.02$ for the photodissociation quantum yield of $C_8F_{17}CHO$. While there is no available UV

spectrum for C₈F₁₇CHO, spectra of CF₃CHO, C₂F₅CHO, C₃F₇CHO, and C₄F₉CHO are available (8). The spectra are similar in shape and have a maximum absorption at 305-310 nm. There is a systematic increase in the intensity of absorption with size of the fluorinated chain up to C₃F₇CHO, but relatively little difference between C₃F₇CHO and C₄F₉CHO. We assume that the UV spectrum of C₄F₉CHO (8) serves as a good model for that of C₈F₁₇CHO. As with CH₃CHO, the photolysis of C₈F₁₇CHO in the troposphere is expected to proceed via C-C bond scission. The resulting C₈F₁₇ radical will add O₂ and can not be a source of C₈F₁₇COOH but can undergo reactions leading to formation of shorter chain perfluorocarboxylic acids, C_xF_{2x+1}COOH (x=1-7) (9).

There are no available kinetic data for the reaction of OH radicals with C₈F₁₇CHO. Kinetic data are available at ambient temperature (296-298 K) for reaction of OH with CF₃CHO (10,11,4,12), C₂F₅CHO (13,12), C₃F₇CHO (12), and C₄F₉CHO (12). Within the experimental uncertainties, there is no discernable effect of the C_xF_{2x+1} chain length on the reactivity of C_xF_{2x+1}CHO towards OH radicals (12). Taking an average of the published data (except reference 11 which is less precise, but consistent with, the body of data) we arrive at a value of $k(\text{OH} + \text{C}_x\text{F}_{2x+1}\text{CHO}) = 6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Assuming an E_a/R term = 1000 gives $k(\text{OH} + \text{C}_8\text{F}_{17}\text{CHO}) = 1.7 \times 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reaction with OH gives an acyl radical, C₈F₁₇C(O). Based upon the behavior of CH₃C(O) and CF₃C(O) radicals we assume that the atmospheric fate of C₈F₁₇C(O) radicals is addition of O₂ to give the acylperoxy radical C₈F₁₇C(O)O₂ which will react with either NO, NO₂, or HO₂.



As described above, we assume that the reactions of $C_8F_{17}C(O)O_2$ with NO and NO_2 have the same kinetics and mechanism as the corresponding reactions of $CH_3C(O)O_2$ radicals (6). Reaction with NO will give NO_2 and $C_8F_{17}O_2$ radicals.



It has been shown by Sulbaek Andersen et al. (14,15) that the reaction of $C_xF_{2x+1}C(O)O_2$ ($x=1-4$) with HO_2 radicals in 100-700 Torr of air, or O_2 , diluent at 296 K proceeds by three pathways leading to formation of $C_xF_{2x+1}C(O)OH$ and O_3 , $C_xF_{2x+1}C(O)OOH$ and O_2 , and $C_xF_{2x+1}C(O)O$ radicals, OH radicals and O_2 . The pathway leading to $C_xF_{2x+1}C(O)OOH$ and O_2 is of minor (<3%) importance for the larger radicals and we assume it is of negligible importance for $C_8F_{17}C(O)O_2$. The yield of $C_xF_{2x+1}C(O)OH$ decreases with increasing size of the $C_xF_{2x+1}C(O)O_2$ radical and appears to tend towards a limit of approximately 10% for large ($x > 3$) $C_xF_{2x+1}C(O)O_2$ radicals. For simplicity we assume here that the $C_8F_{17}C(O)OH$ acid yield in the $C_8F_{17}C(O)O_2 + HO_2$ reaction is the same as that observed in the reactions of $C_3F_7C(O)O_2$ and $C_4F_9C(O)O_2$ radicals with HO_2 radicals, i.e., 10%. Furthermore, we assume that this yield is independent of temperature and that the kinetics of the $C_8F_{17}C(O)O_2 + HO_2$ reaction are the same as those for $CH_3C(O)O_2 + HO_2$ reaction.

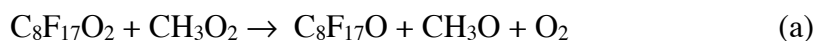
2.1.4 Atmospheric fate of $C_8F_{17}O_2$ radicals

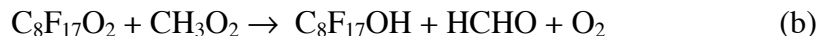
The sole atmospheric fate of $C_8F_{17}C(O)O$ radicals formed in the $C_8F_{17}C(O)O_2 + HO_2$ and $C_8F_{17}C(O)O_2 + NO$ reactions is elimination of CO_2 to give C_8F_{17} radicals which will add O_2 to give $C_8F_{17}O_2$ radicals. As with other peroxy radicals, the atmospheric fate of

$C_8F_{17}O_2$ will be reaction with NO, NO_2 , HO_2 , and other peroxy radicals (e.g., CH_3O_2). The reaction of $C_8F_{17}O_2$ radicals with NO and HO_2 are assumed to proceed at the same rate as the corresponding reactions of CH_3O_2 radicals. Reaction with NO_2 gives a thermally unstable peroxyxynitrate which will decompose rapidly to regenerate the reactants (this reaction need not be included in the model). Evidence has been presented that the reaction of $C_8F_{17}O_2$ with alkyl peroxy radicals bearing an α -hydrogen atom leads to the formation of the alcohol $C_8F_{17}OH$ which will undergo heterogeneous decomposition via elimination of HF (16,17) to give the acid fluoride ($C_7F_{15}C(O)F$) which undergoes hydrolysis to give the corresponding acid, $C_7F_{15}C(O)OH$. CH_3O_2 is the most abundant α -hydrogen containing peroxy radical in the atmosphere. An estimate of the rate constant for reaction of $C_8F_{17}O_2$ with CH_3O_2 can be obtained by assuming (i) all $C_xF_{2x+1}O_2$ radicals react with CH_3O_2 at the same rate and (ii) the rate of the cross reaction can be estimated from the rates of the self-reactions. Kinetic data are available for the self reactions of CF_3O_2 and CH_3O_2 radicals and the cross reaction rate can be estimated using the following expression (18):

$$k(CF_3O_2 + CH_3O_2) = 2\sqrt{k(CF_3O_2 + CF_3O_2) \times k(CH_3O_2 + CH_3O_2)}$$

Using $k(CF_3O_2 + CF_3O_2) = 1.7 \times 10^{-12}$ (19) and $k(CH_3O_2 + CH_3O_2) = 3.5 \times 10^{-13}$ (6) gives $k(CF_3O_2 + CH_3O_2) = k(C_8F_{17}O_2 + CH_3O_2) = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K. There are few available data with which to estimate the temperature dependence of the kinetics, or branching ratio, of the $C_8F_{17}O_2 + CH_3O_2$ reaction. For the purposes of the present work we adopt a temperature dependence for the overall reaction and branching ratio which is the same as that for the CH_3O_2 self reaction.





Hence, $(k_a+k_b) = 4.0 \times 10^{-13} \exp(390/T)$ and $k_a/k_b = 26.2 \exp(-1130/T)$ from which we derive $k_a = 2.7 \times 10^{-12} \exp(-470/T)$ and $k_b = 1.0 \times 10^{-13} \exp(660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The alcohol $\text{C}_8\text{F}_{17}\text{OH}$ will undergo HF elimination and hydrolysis to give the acid $\text{C}_7\text{H}_{15}\text{COOH}$ (PFOA) on a time scale similar to that for hydrolysis of COF_2 in the atmosphere, i.e., approximately 5 days (pseudo first order rate = $2.3 \times 10^{-6} \text{ s}^{-1}$) (20). The alkoxy radical, $\text{C}_8\text{F}_{17}\text{O}$, formed by reaction of the $\text{C}_8\text{F}_{17}\text{O}_2$ peroxy radical with either NO, HO_2 , or CH_3O_2 will eliminate COF_2 and form the smaller fluorinated alkyl peroxy radical $\text{C}_7\text{F}_{15}\text{O}_2$. As with $\text{C}_8\text{F}_{17}\text{O}_2$, the dominant atmospheric fate of $\text{C}_7\text{F}_{15}\text{O}_2$ will be conversion into the corresponding alkoxy radical, $\text{C}_7\text{F}_{15}\text{O}$ (via reaction with NO, HO_2 , and CH_3O_2 radicals). The alkoxy radical $\text{C}_7\text{F}_{15}\text{O}$ will eliminate COF_2 and form the next smallest fluorinated alkyl peroxy radical $\text{C}_6\text{F}_{13}\text{O}_2$. A sequence of reactions ensues leading to the "unzipping" of the molecule via successive elimination of COF_2 units (see bottom right in Figure 1). Each time through the cycle a fraction of the $\text{C}_x\text{F}_{2x+1}\text{O}_2$ radicals will react with CH_3O_2 giving $\text{C}_x\text{F}_{2x+1}\text{OH}$ and hence the $\text{C}_{x-1}\text{F}_{2x-1}\text{COOH}$ acid. If we assume that the atmospheric chemistry of $\text{C}_x\text{F}_{2x+1}\text{O}_2$ radicals is the same as that of $\text{C}_8\text{F}_{17}\text{O}_2$ then the yields of $\text{C}_x\text{F}_{2x+1}\text{COOH}$ ($x=1-6$) will be the same as that for $\text{C}_7\text{F}_{15}\text{COOH}$. The final step is formation of CF_3 radicals which are then converted into CF_3O radicals and hence into COF_2 .

The total perfluorocarboxylic acid yield from the atmospheric oxidation of 8:2 FTOH will be approximately $Y_{\text{C}_8\text{F}_{17}\text{COOH}} + 7 Y_{\text{C}_7\text{F}_{15}\text{COOH}}$ where $Y_{\text{C}_8\text{F}_{17}\text{COOH}}$ and $Y_{\text{C}_7\text{F}_{15}\text{COOH}}$ are the molar yields of $\text{C}_8\text{F}_{17}\text{COOH}$ and $\text{C}_7\text{F}_{15}\text{COOH}$ estimated using the model described above.

2.1.5 Wet and dry deposition rates used in the model

2.1.5.1 C₈F₁₇CH₂CH₂OH

Based upon an estimated dimensionless air-water partition constant (K_{AW}) of 316 the lifetime of 8:2 FTOH with respect to wet deposition was assessed to be 2.6 million years (1). Lei et al. (21) have recently measured $K_{AW} = 20.42 \pm 2.09$ for 8:2 FTOH enabling us to reevaluate the importance of wet deposition using expression (I) (22,23).

$$k_{WD} = (R_r E e^{(-z/Z_x)}) / Z_x (H^* + \Phi) \quad (I)$$

k_{WD} is the rate of wet deposition, R_r is the annual rainfall rate, taken to be 3.2×10^{-8} m/s, E is the enhancement factor due to evaporation of falling rain droplets, taken to be 1.33, z is the characteristic height of stratus clouds (3.5 km), Z_x is the scale height of the 8:2 FTOH (2.3 km), H^* is K_{AW} , and Φ is the fraction of air volume occupied by liquid water.

Equation (I) gives $k_{WD} = 1.98 \times 10^{-13} \text{ s}^{-1}$ which yields an expected lifetime from equation (II) of 160,000 years.

$$\tau_{WD} = 1/k_{WD} \quad (II)$$

Ellis et al. (1) reported a dry deposition lifetime 8.4 years. Lei et al. (21) have suggested from the volatility and octanol-air (K_{OA}) partition coefficient that 8:2 FTOH will remain predominately in the gas phase, even at cold temperatures. Loss of 8:2 FTOH by wet or dry deposition will be of negligible importance and was not included in the model.

2.1.5.2 C₈F₁₇CH₂CHO

FTOHs have vapor pressures and K_{AW} values which are 1-2 orders of magnitude larger than their hydrocarbon counterparts (21,24). Decanal has a K_{aw} value of 4.75×10^{-2} (25) and hence the K_{aw} for C₈F₁₇CH₂CHO will be in the range 0.5 – 5. Substituting into

equation (I) gives a rainout rate of $8.08 \times 10^{-12} - 8.08 \times 10^{-13} \text{ s}^{-1}$ corresponding to a lifetime with respect to wet deposition, see equation (II), of 4,000 – 40,000 years.

The dry deposition velocity of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ to a body of water can be estimated using equation (III).

$$v_d = 1/(r_a + r_b + r_s) \quad \text{(III)}$$

$r_a + r_b$ are resistances to transport to the layer and are taken to be 192 and 67 s m^{-1} , respectively. The term r_s is the surface resistance of a gaseous substance and can be further defined as $K_{AW} \cdot r_w$ in which r_w is 105 s m^{-1} . The dry deposition velocity for the $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ was calculated to be $(1.28 - 3.21) \times 10^{-3} \text{ m s}^{-1}$. For the purposes of the present work we adopted a dry deposition velocity for $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ near the midpoint of the range given above, $1.9 \times 10^{-3} \text{ m s}^{-1}$.

The lifetime with respect to dry deposition can be estimated from the deposition velocity using equations (IV) and (V):

$$k_{DD} = v_d/Z_x \quad \text{(IV)}$$

$$\tau_{DD} = 1/k_{DD} \quad \text{(V)}$$

Z_x is the depth of the atmosphere within which $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ is formed. $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ is produced from the oxidation of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$ which occurs on a time scale of the order of 10 days. Hence, $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ will be formed throughout the troposphere, Z_x is approximately 14 km, and the lifetime of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ with respect to dry deposition is of the order of 70 days. The actual lifetime with respect to dry deposition in the IMPACT model was 48 days (see Section 2.2 of the main paper).

It should be noted that aldehydes undergo hydration in the aqueous phase to yield geminal diols and this reaction is expected to be enhanced by partial fluorination. This

chemical reaction would enhance the water solubility of $C_8F_{17}CH_2CHO$ when compared with the hydrocarbon counterpart. However, greatly offsetting this increased water solubility is the increased hydrophobicity of the polyfluorinated chain when compared with the hydrocarbon. Thus, hydration is not expected to impact the overall gas-water partition of $C_8F_{17}CH_2CHO$ significantly.

2.1.5.3 $C_8F_{17}CHO$

Estimation of the significance of wet and dry deposition for $C_8F_{17}CHO$ is complicated by the lack of physico-chemically relevant parameters for perfluorinated aldehydes. It is known that equivalent chain length perfluorocarbons have essentially the same vapor pressure (V_p) but are much less soluble than non-fluorinated hydrocarbons (e.g. C_2F_6 and C_2H_6) (5). It seems unlikely that wet and dry deposition are significant loss mechanisms for $C_8F_{17}CHO$ and these processes were not included in the model.

2.1.5.4 $C_8F_{17}COOH$ (PFNA) and $C_7F_{15}COOH$ (PFOA)

Rates for wet and dry deposition of PFCAs have been estimated by Franklin (26) and Hurley et al. (27). Franklin (26) estimated a wet deposition lifetime of 6.2 days (half-life of 4.3 days) for PFOA. As noted by Franklin (26), this value is based upon the assumption that PFOA is emitted into the atmosphere and if PFOA is formed in the atmosphere it is likely to have a lifetime longer than 6.2 days. Wet and dry deposition rates for PFOA and PFNA used in the IMPACT model were based on an effective Henry's law coefficient (defined as the ratio of gas-phase to the sum of direct and dissociated aqueous species) of $2.46 \times 10^3 \text{ mol L}^{-1} \text{ atm}^{-1}$ from Franklin (26) and a global average dry deposition velocity of 0.19 cm s^{-1} . The wet and dry deposition used in the IMPACT model resulted in lifetimes of 17 days and 48 days with respect to wet and

dry deposition respectively, for a combined lifetime of 12 days. This is consistent with the estimate by Hurley et al. (27) of a combined wet and dry deposition lifetime of approximately 10 days.

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