

SUPPORTING INFORMATION

Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis and Hydration

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Computational Methods

All compounds in the present study were modelled using *Gaussian 03* with the WebMO user interface (1). Their structures and acronyms are given in Figure 1. All computations were performed using Density Functional Theory (DFT) using B3LYP functionals. All compounds were first geometry optimized in the gas phase with the 3-21G basis set and then re-optimized using the 6-31G(d,p) basis set. Every structure's vibrational modes were examined to ensure no imaginary frequencies were found. Each optimized structure using 6-31G(d,p) was subjected to a single point molecular energy calculation in both the gas and aqueous phases using the 6-311++G(d,p) basis set. For aqueous phase calculations, the default PCM solvent model in *Gaussian 03* was used. Molecular orbital calculations were performed in regular population mode using the 6-311++G(d,p) basis set in the gas phase.

The equilibrium constants for hydration (K_{hyd}) for each compound were calculated using the relative method outlined by Gomez-Bombarelli et al (2). For perfluoro-2-methyl-3-pentanone (PFMP), both the relative method of Gomez-Bombarelli et al. as well as a training set method was used. The training set consisted of fluoroacetone, trifluoroacetone and hexafluoroacetone because all three compounds have literature K_{hyd} values. In the relative method, acetone was chosen as the group reference compound for purposes of calculating $\log K_{\text{hyd}}$. In this manner, the calculated and literature K_{hyd} values for acetone are used to compute K_{hyd} for a compound of choice to minimize any systemic computational errors. The energies chosen in the present study were the computed B3LYP energies of each compound with the unscaled zero point energies (ZPEs) from the 6-31G(d,p) basis set added.

The formulas used to calculate $\log K_{\text{hyd}}$ for each compound were as follows:

$$\Delta E = E_{\text{hydrate}} + E_{\text{acetone}} - E_{\text{carbonyl}} - E_{\text{acetonehydrate}} \quad (\text{S1})$$

$$\log K_{\text{hyd}} = \log K_{\text{acetone}} - \Delta E / (\ln 10)(RT) \quad (\text{S2})$$

where $\log K_{\text{acetone}}$ is the literature hydration constant of acetone (-2.85) (3). All temperatures were 298 K.

When computing $\log K_{\text{hyd}}$ for PFMP using the above relative method, all that is needed is the computed B3LYP energies of acetone, PFMP and their respective hydrates using whatever solvent is desired. However, to reduce systematic errors even further, a training set can be developed whereby $\log K_{\text{hyd}}$ is computed using the above method for similar compounds where literature values of $\log K_{\text{hyd}}$ are already available. In the present study, fluoroacetone, trifluoroacetone and hexafluoroacetone were chosen to construct the training set. Then, a calibration curve can be plotted to relate the literature values to the computed values. Finally, the most accurate hydration constant for PFMP can be determined.

Computational Results

The training set consisted of fluoroacetone, trifluoroacetone and hexafluoroacetone because literature values for hydration exist for these molecules (3) and they share structural similarity with PFMP. In addition, B3LYP energies were computed using the 6-311++G(d,p) basis set for both the gas phase and aqueous phase, leading to four possible values of K_{hyd} for PFMP depending on which method and solvent model was used for the calculation. This results in the range of values for K_{hyd} as given in the body of the paper.

Figure S1. Chemical structures of all compounds modelled computationally using DFT/B3LYP

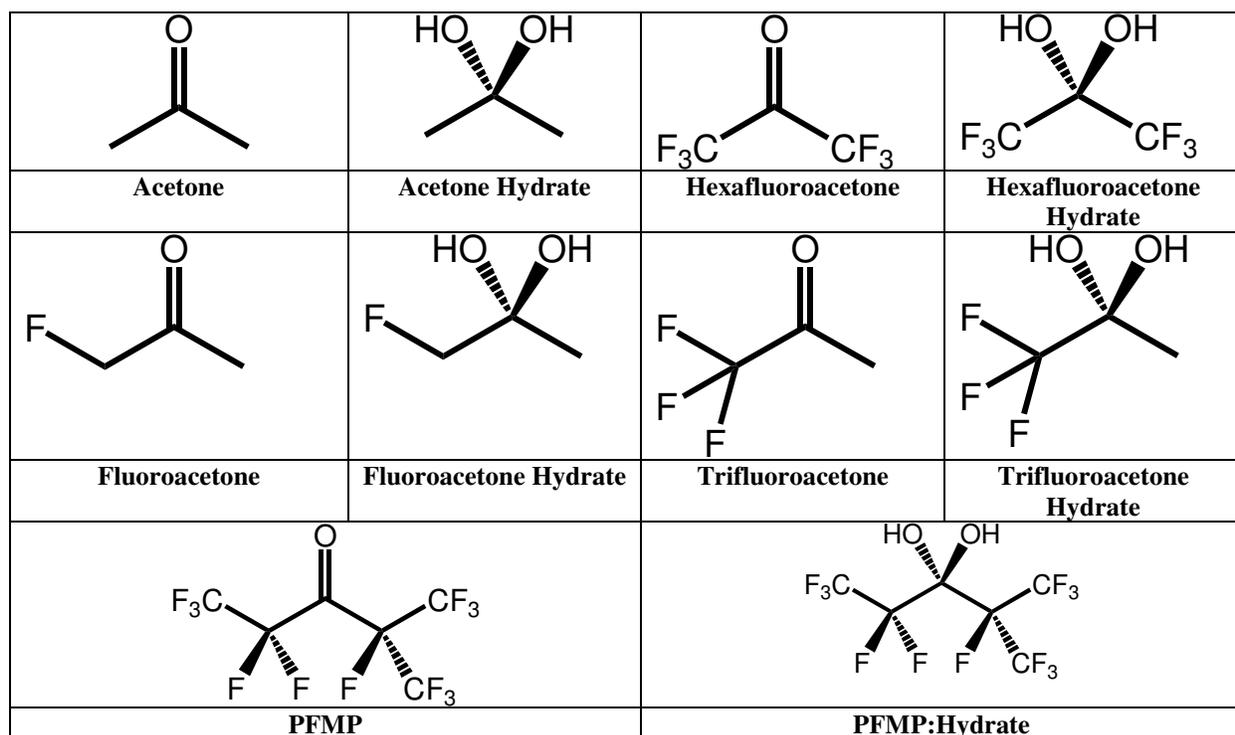


Table S1. Computationally derived K_{hyd} values using B3LYP/6-311++G(d,p) in the gas phase

Compound	Training Set Method $\log K_{\text{hyd}}$	Relative Method $\log K_{\text{hyd}}$	Lit. $\log K_{\text{hyd}}$
Fluoroacetone	na	-0.16	-0.78
Trifluoroacetone	na	0.80	1.54
Hexafluoroacetone	na	5.39	6.08
PFMP	-2.09	-1.76	none

Table S2. Computationally derived K_{hyd} values using B3LYP/6-311++G(d,p) in the aqueous phase using the PCM solvent model

Compound	Training Set Method log K_{hyd}	B3LYP Energy Relative Method log K_{hyd}	Lit. log K_{hyd}
Fluoroacetone	na	-1.73	-0.78
Trifluoroacetone	na	2.56	1.54
Hexafluoroacetone	na	7.71	6.08
PFMP	-0.43	-0.85	none

Figure S2. Computationally derived and literature log K_{hyd} values for training set compounds and PFMP using B3LYP/6-311++G(d,p) in both gas and aqueous phases

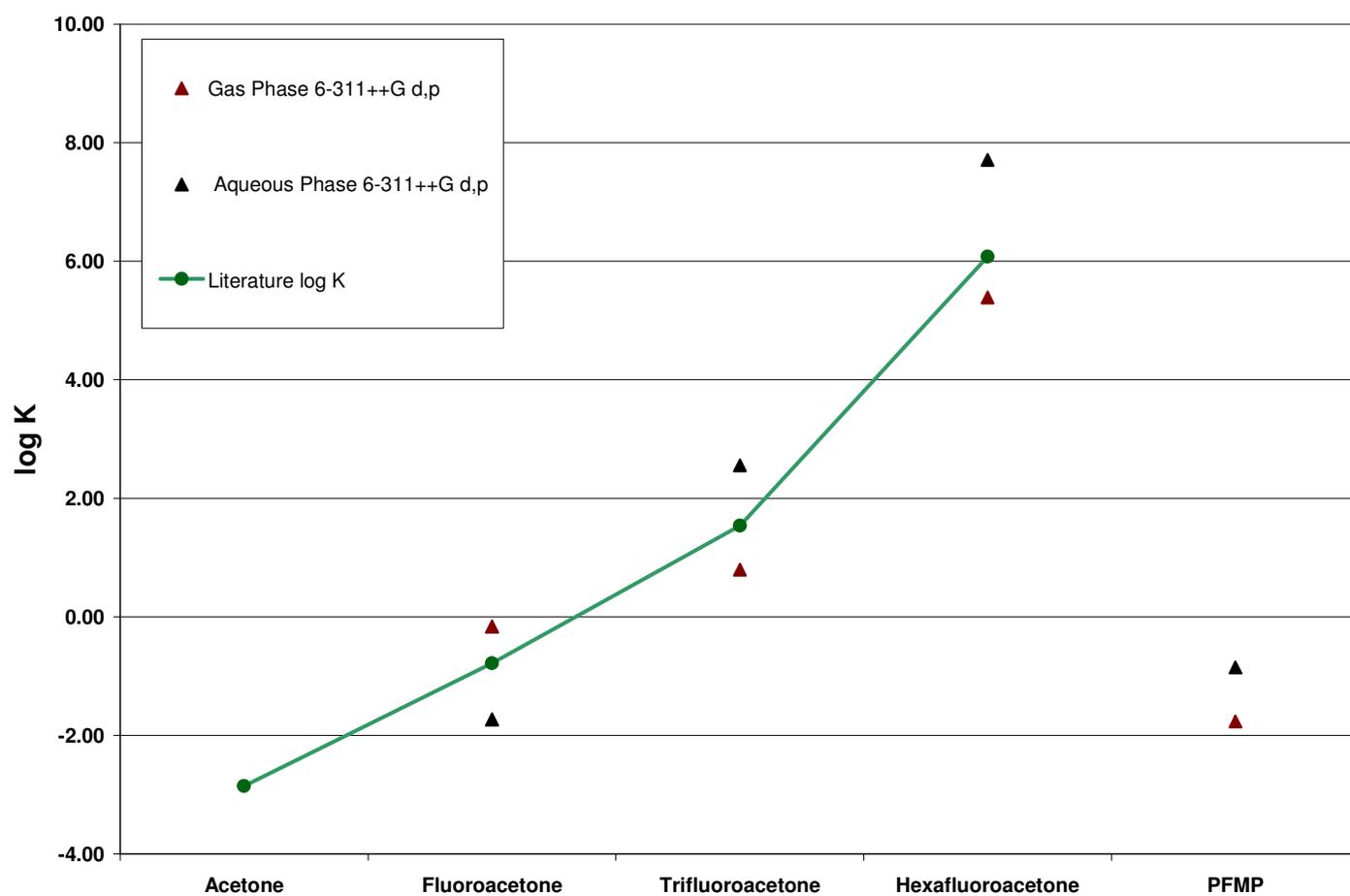
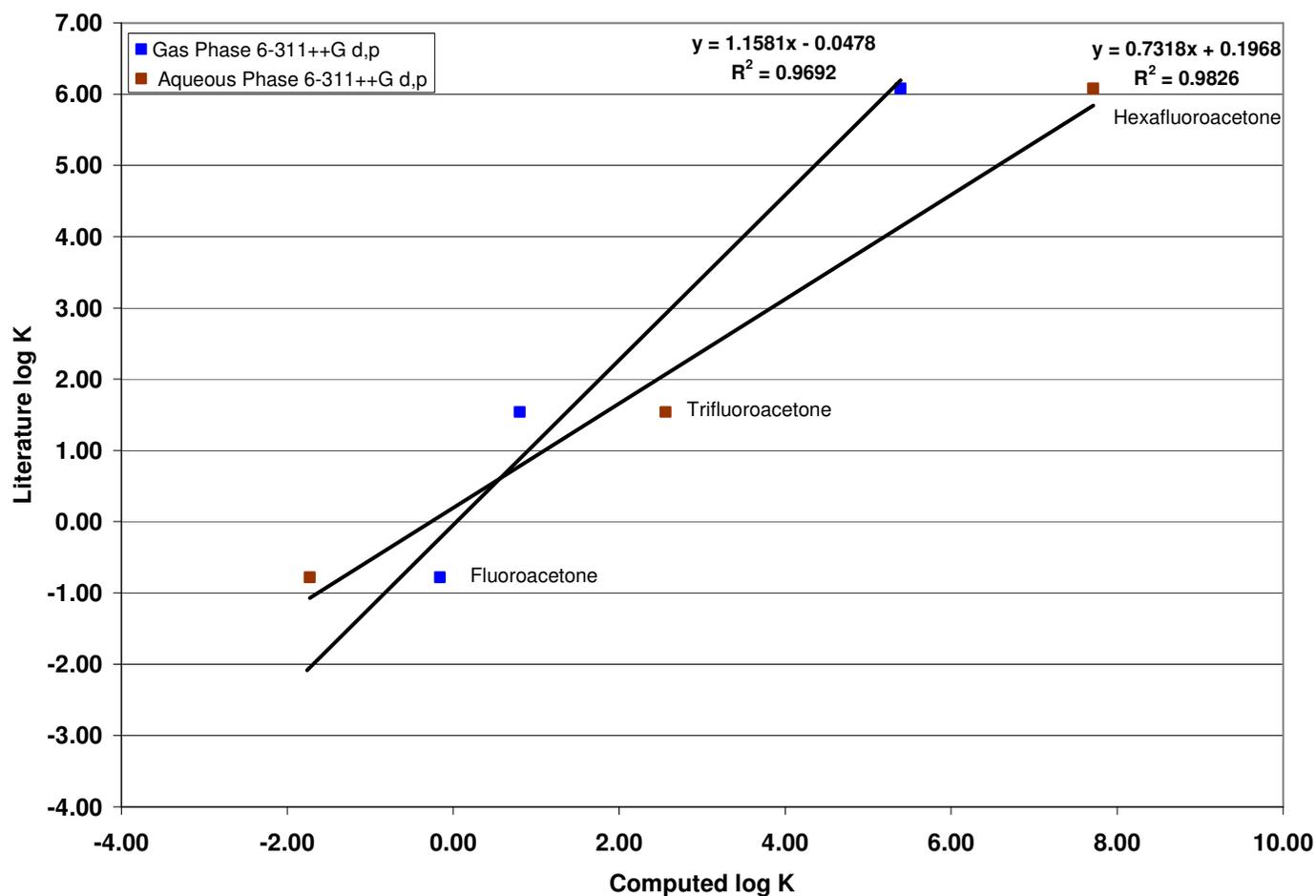


Figure S3. Linear calibrations of training set literature $\log K_{\text{hyd}}$ versus computationally derived $\log K_{\text{hyd}}$ values using B3LYP/6-311++G(d,p) in both the gas and aqueous phases.



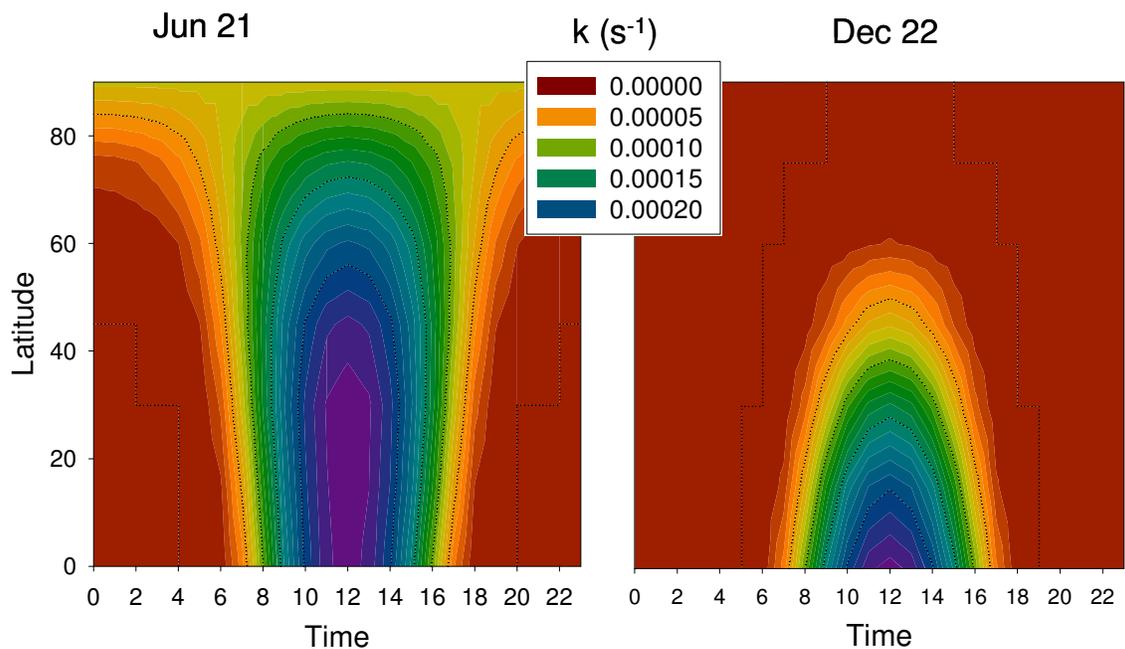
As shown in the Figure 2, the relative method of Gomez-Bombarelli et al. gives hydration constants reasonable close to the literature values for fluoroacetone, trifluoroacetone and hexafluoroacetone.

Hence the $\log K_{\text{hyd}}$ values for PFMP range from -0.43 to -2.09, showing the relative unimportance of hydration for the environmental fate of PFMP.

Table S3. Rate constants and lifetimes for PFMP based on latitude and time of year from the TUV model using the literature quantum yield of photolysis as 0.043.

Latitude	24 Hour Average Rate Constant (10^{-7} s^{-1})					Annual Average
	Dec 22	Mar 22	Jun 21	Sept 23	Annual Average	Lifetime (days)
90° N	0.00	0.65	32	0.57	8.2	14
75° N	0.00	4.5	32	4.3	10	11
60° N	0.71	13	33	13	15	7.8
45° N	5.9	21	35	21	21	5.6
30° N	15	27	35	27	26	4.5
15° N	23	31	33	31	29	3.9
0°	30	32	28	32	31	3.8
15° S	35	31	22	31	30	3.9
30° S	37	27	14	27	26	4.4
45° S	38	21	5.5	21	21	5.4
60° S	36	13	0.66	13	15	7.5
75° S	34	4.3	0.00	4.4	11	11
90° S	34	0.53	0.00	0.59	9.2	13

Figure S4. Contour plots showing the photolytic rate constants of PFMP in the northern hemisphere as derived by the TUV model assuming a quantum yield of 0.043.



The Relative Importances of Photolysis and Hydrolysis: Environmental Modelling

To demonstrate the relative importances of photolysis and hydrolysis in the atmosphere, the modelling methods of Cahill and Mackay (4) were used. In short, the rate constants of both reactions were combined with PFMP's physical properties and the amount of liquid water in the atmosphere to determine the relative rates of both.

The rate of PFMP degradation (R) in the atmosphere due to direct photolysis is given by the following equation:

$$R_{\text{photolysis}} = -C_A V_A k_{\text{photolysis}} \quad (\text{S3})$$

where C_A is the concentration of PFMP in the atmosphere, V_A is the volume of air and $k_{\text{photolysis}}$ is the first order photolytic rate constant. $k_{\text{photolysis}}$ will vary depending on time of day, latitude and prevailing weather

conditions. However, a typical value for a mid-latitude summer can be taken as $35 \times 10^{-7} \text{ s}^{-1}$ from the TUV modelling data.

The photolysis equation reduces to:

$$R_{\text{photolysis}} = -C_A V_A (35 \times 10^{-7} \text{ s}^{-1}) \quad (\text{S4})$$

To model the hydrolysis reaction of PFMP, it is necessary to include the air-water partitioning coefficient, K_{AW} since equilibrium conditions will be assumed for this calculation. For PFMP, $K_{\text{AW}} = 5300$. The rate of hydrolysis in the atmosphere is given by the following equation:

$$R_{\text{hydrolysis}} = -C_W (F_W V_A) k_{\text{hydrolysis}} \quad (\text{S5})$$

where C_W is the concentration of PFMP in the aqueous phase, F_W is the fraction of liquid water in the atmosphere, V_A is the volume of the air parcel and $k_{\text{hydrolysis}}$ is the pseudo first order rate constant for the hydrolysis reaction at the pH being considered. Atmospheric water typically has a pH of 5.6 so $k_{\text{hydrolysis}} = 4.2 \times 10^{-4} \text{ s}^{-1}$. The fraction of liquid water in the atmosphere, F_W is 4.5×10^{-8} as indicated by De Bruyn et al. (5) The concentration of PFMP in water assuming equilibrium conditions is given by $C_W = C_A / K_{\text{AW}}$.

The rate of hydrolysis equation then becomes:

$$R_{\text{hydrolysis}} = -(C_A / 5300) (4.5 \times 10^{-8} V_A) (4.2 \times 10^{-4} \text{ s}^{-1}) \quad (\text{S6})$$

Since both the rates of hydrolysis and photolysis include only C_A and V_A , they will cancel out when the ratio is taken to find the importance of photolysis versus hydrolysis:

$$R_{\text{photolysis}} / R_{\text{hydrolysis}} = \text{approx. } 980,000,000:1 \quad (\text{S7})$$

Figure S5. ^{19}F NMR of PFMP (neat) with expansions on each signal to show nuclei coupling patterns.

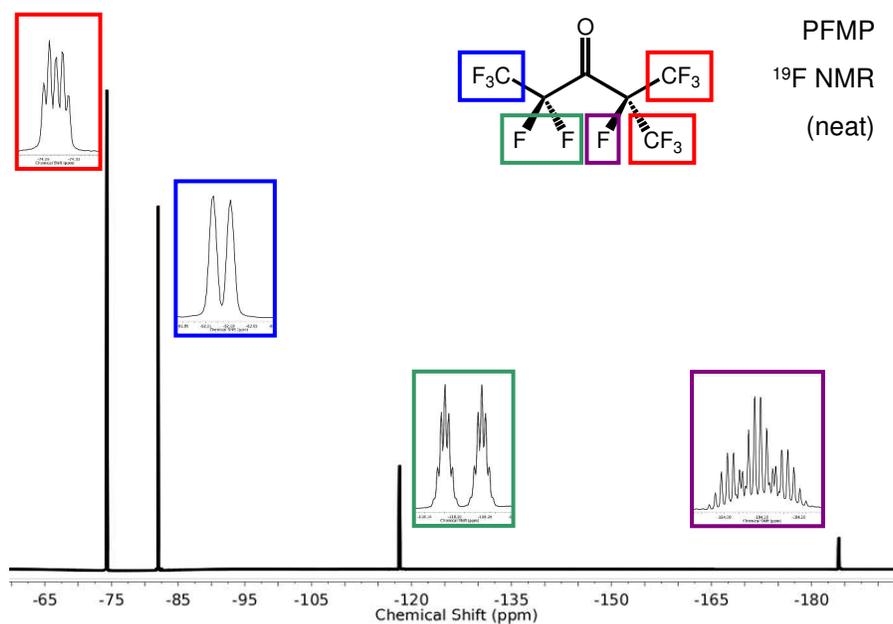
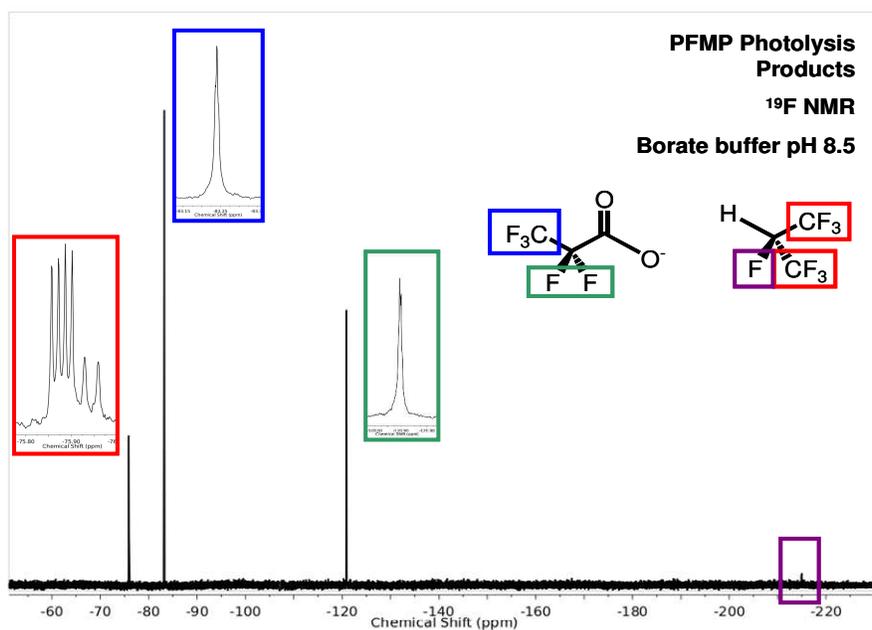


Figure S6. ^{19}F NMR of PFMP photolysate at completion of reaction (borate buffer pH 8.5) with expansions on selected signals to show nuclei coupling patterns.



Prediction of PFPrA concentrations in precipitation

This simple model makes the assumption that 1000 t of PFMP are produced each year in the United States and that 3% is emitted into the atmosphere each year, corresponding to 30 t yr^{-1} .

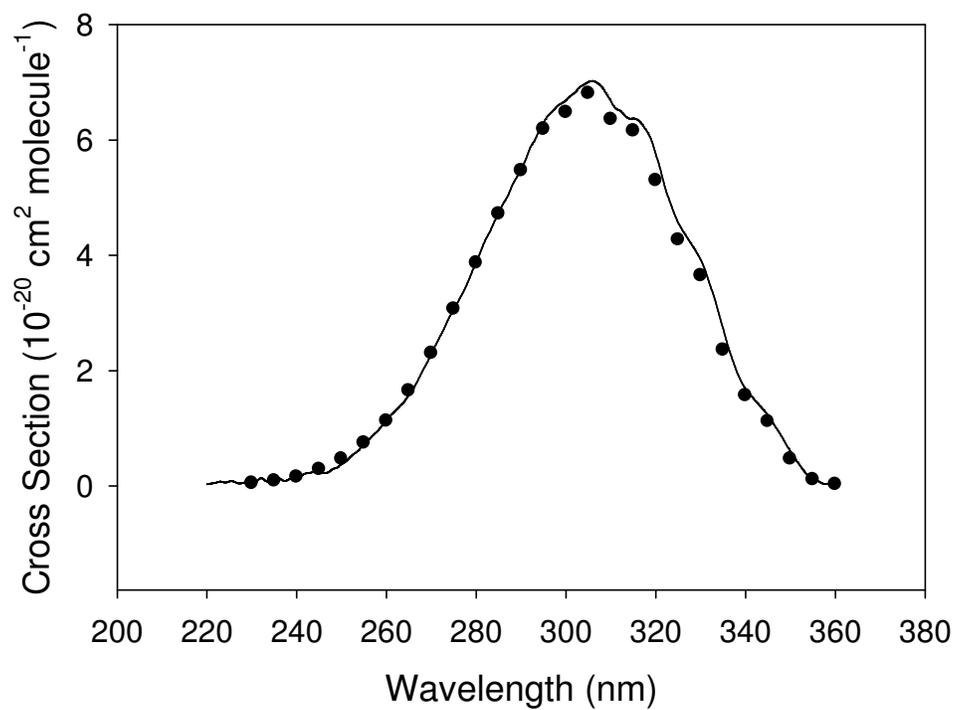
It is also assumed that due to an average atmospheric lifetime of 1 week due to photolysis, that all 30 t emitted each year will degrade. The yield of PFPrA from photolysis is assumed to be 24% due to the experimental branching ratio of the $\text{C}_2\text{F}_5\text{C}(\text{O}) + \text{HO}_2$ reaction (6). The actual yield of PFPrA will likely be lower since a competing reaction in the presence of NO_x will drive a competing reaction that will “unzip” the perfluorinated chain and PFPrA can no longer be produced. Therefore, we will derive an upper limit for PFPrA production by photolysis.

Each year, 30 t PFMP degrades to produce PFPrA. Taking into account the molecular weights of PFMP and PFPrA as well as the 24% branching ratio, it can be shown that 3.7 t PFPrA will be atmospherically produced annually.

It can also be assumed that PFPrA, due to its low vapour pressure and high water solubility, will be quantitatively scavenged by precipitation and deposited from the atmosphere. The total annual precipitation in the continental United States is approximately $6.5 \times 10^{15} \text{ L}$ (7). This corresponds to a maximal PFPrA concentration in rainfall of 0.6 ng L^{-1} .

The above calculation assumes PFMP will only be distributed within the continental United States. With a lifetime of one week however, PFMP will be subjected to long range transport. If total precipitation in Canada is combined with the United States (annual precipitation in Canada is approximately $5.5 \times 10^{15} \text{ L}$ (8)), this lowers the PFPrA concentration to 0.3 ng L^{-1} .

Figure S7. Measured UV-vis absorption cross section for PFK; 5 nm moving average of 1 nm, measured data from 218 – 382 nm (solid line); data from Taniguchi et al. (9) (dots).



References for Supporting Information

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