Environmental Science & Technology

ARTICLE

pubs.acs.org/est

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

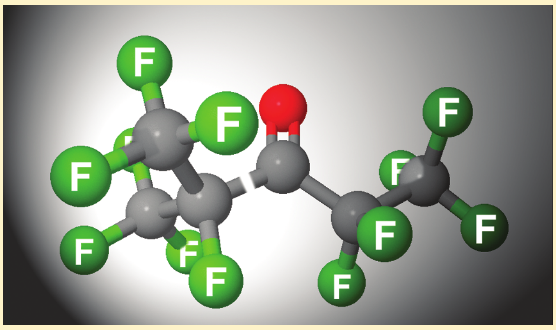
Derek A. Jackson,[†] Cora J. Young,[†] Michael D. Hurley,[‡] Timothy J. Wallington,[‡] and Scott A. Mabury*,[†]

[†]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON, Canada M5S 3H6

[‡]Ford Motor Company, Mail Drop SRL-3083, Dearborn, Michigan, 48121 United States

S Supporting Information

ABSTRACT: Perfluorinated carboxylic acids are widely distributed in the environment, including remote regions, but their sources are not well understood. Perfluoropropionic acid (PFPrA, $CF_3CF_2C(O)OH$) has been observed in rainwater but the observed amounts can not be explained by currently known degradation pathways. Smog chamber studies were performed to assess the potential of photolysis of perfluoro-2-methyl-3-pentanone (PFMP, $CF_3CF_2C(O)CF(CF_3)_2$), a commonly used fire-fighting fluid, to contribute to the observed PFPrA loadings. The photolysis of PFMP gives $CF_3CF_2C{\cdot}(O)$ and ${\cdot}CF(CF_3)_2$ radicals. A small (0.6%) but discernible yield of PFPrA was observed in smog chamber experiments by liquid chromatography—mass spectrometry offline chamber samples. The Tropospheric Ultraviolet—Visible (TUV) model was used to estimate an atmospheric lifetime of PFMP with respect to photolysis of 4—14 days depending on latitude and time of year. PFMP can undergo hydrolysis to produce PFPrA and CF_3CFHCF_3 (HFC-227ea) in a manner analogous to the Haloform reaction. The rate of hydrolysis was measured using ^{19}F NMR at two different pHs and was too slow to be of importance in the atmosphere. Hydration of PFMP to give a geminal diol was investigated computationally using density functional theory. It was determined that hydration is not an important environmental fate of PFMP. The atmospheric fate of PFMP seems to be direct photolysis which, under low NO_x conditions, gives PFPrA in a small yield. PFMP degradation contributes to, but does not appear to be the major source of, PFPrA observed in rainwater.



INTRODUCTION

Perfluorinated carboxylic acids (PFCAs) are ubiquitous in biotic[1] and abiotic environments.[2,3] Longer-chain (>C_8) PFCAs are bioaccumulative[4] and have attracted substantial research interest. Precipitation measurements by Scott et al.[3] have demonstrated that short-chain PFCAs, notably trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA), dominate the PFCA profile. Although these smaller compounds are not expected to bioaccumulate and are not believed to represent a threat to ecosystems, their source is unclear and requires study. Thermolysis of fluoropolymers has been suggested as a potential source of TFA observed in rainwater.[5] Other sources of TFA include the atmospheric oxidation of hydrofluorocarbons[6,7] and polyfluorinated compounds.[8,9] Small yields of PFPrA have been proposed from thermolysis of fluoropolymers and atmospheric oxidation of fluorotelomer alcohols[5,8,9] but do not explain the levels of PFPrA observed in precipitation.

Perfluoro-2-methyl-3-pentanone (PFMP) is a fire protection fluid, marketed as Novec 1230 by 3M. It is a replacement for chlorofluorocarbons (CFCs) and Halons, which deplete stratospheric ozone. The atmospheric lifetime of PFMP from previous work seems to be determined by photolysis and is approximately 1 week.[10,11] PFMP does not contribute to stratospheric ozone depletion and has a negligible global warming potential.[10,11] The major photolysis products are $CF_3C(O)F$ and COF_2.[10] The atmospheric fate of $CF_3C(O)F$ is hydrolysis to yield TFA. It is possible that chemistry in remote environments following the photolysis of PFMP would give small yields of PFPrA or isoperfluorobutanoic acid (*i*-PFBA) via reactions of the corresponding perfluoroacyl radicals with HO_2 radicals.[12,13]

In addition to photolysis, hydration or abiotic hydrolysis may be a significant sink of PFMP in the environment. In the hydration reaction, PFMP would react either reversibly or irreversibly with water to form a geminal diol which would shut down the photolysis pathway. Ketones are typically unreactive toward hydrolysis because the leaving group after nucleophilic attack is an aliphatic carbanion. Carbanions are highly basic and are not good leaving groups. However, hydrolysis of PFMP gives

Special Issue: Perfluoroalkyl Acid

Received: December 28, 2010
Accepted: March 25, 2011
Revised: March 15, 2011
Published: April 05, 2011

a perfluorinated carbanion which, because the fluorine atoms stabilize the departing carbanion through hyperconjugation, is a much better leaving group. This effect is the basis of the well-known Haloform reaction, one of the oldest organic reactions known.[14]

Applying the Haloform reaction mechanism to hydrolysis of PFMP should give PFPrA and CF_3CFHCF_3 (HFC-227ea). HFC-227ea is a long-lived greenhouse gas and its formation would be problematic. A detailed understanding of the rate and products of PFMP hydrolysis under environmentally relevant conditions is clearly desirable.

The present work had three goals: (i) to confirm the rate of atmospheric photolysis of PFMP and to investigate the possible formation of PFPrA, (ii) to determine whether hydrolysis of PFMP is of significance in the environment, and (iii) to investigate whether hydration is an environmental fate of PFMP.

EXPERIMENTAL DETAILS

Measurements of UV Spectra and Calculations of Photolysis Rates. UV spectra of PFMP in the region 200−400 nm were recorded in a 6-cm cell using a Perkin-Elmer UV/vis spectrometer with a resolution of 1 nm, a slit width of 0.25 nm, and a scan speed of 15 nm min^{-1}. Photolysis rates were estimated using the Tropospheric Ultraviolet−Visible (TUV 4.2) package.[15] All rates were calculated for 0.5 km above the surface. The quantum yield was assumed to be 0.043, as measured by D'Anna et al.[11]

Smog Chamber Methods. Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The reactor was surrounded by 10 fluorescent blacklamps (GE F15T8-BL, maximum emission 360 nm) and 12 sunlamps (GE-FS40, maximum emission 310 nm), which were used to photolyze PFMP. The spectral overlap of the emission of blacklamps and sunlamps and the absorption by PFMP has been discussed by Taniguichi et al.[10] All reagents were obtained from commercial sources. Concentrations of reactants and products were monitored by FTIR 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 m. Photolysis experiments were performed using mixtures containing 0.49−0.62 Torr of PFMP in 50 Torr of oxygen. We chose a diluent pressure of 50 Torr for the photolysis experiments as Taniguichi et al.[10] have established that the photolysis proceeds more rapidly at lower total pressures. After photolysis the reaction mixtures were pressurized to 750 Torr with air and sampled as described below.

The experimental conditions employed in the smog chamber experiments (296 K, 50 Torr total pressure of O_2 diluent, in the absence of water vapor, NO_x, and other important atmospheric constituents) are not the same as the range of conditions in the real atmosphere. However, the chemical processes studied in the chamber are very similar to those which will occur in the real atmosphere. Photolysis of PFMP in the chamber will occur via the same mechanism, the fate of the radicals formed (decomposition and addition of O_2) will be similar, and subsequent reactions of the peroxy radicals are similar to those in the real atmosphere. Hence, the results from such smog chamber experiments shed important light on the behavior of PFMP in the real atmosphere.

Offline Sample Collection and Analysis. Offline samples were collected by bubbling approximately 5 L of chamber air through 10 mL of sodium carbonate solution (pH 11) after dilution of the chamber contents with air (P_T = 750 Torr). Triplicate samples were collected following 45 min of irradiation. Sodium carbonate solutions were acidified to pH 4 using HCl and analyzed using a Waters 616 LC pump and 600 controller with detection by a Micromass Quattro Micro MS/MS detector. Analytes were separated on a Genesis C8 column (2.1 mm × 50 mm × 4 μm) using a 5-min isocratic run of 40% methanol and 60% water, both containing 10 mM ammonium acetate. Triplicate 10 μL injections were made using a Waters 717 autosampler. PFCAs were analyzed using a cone voltage of 17 V and collision energy of 9 eV and the following transitions were monitored: PFBA 213 > 169, PFPrA 163 > 119, and TFA 113 > 69. Analytes were quantified using external calibration.

Hydrolysis Kinetic Experiments. To quantify the rate of PFMP hydrolysis and identify the final products of hydrolysis, ^{19}F NMR was used. The rates of hydrolysis were measured at pH values of 5.6 anad 8.5 to simulate the upper and lower boundaries of realistic environmental pH conditions. To achieve this, either 50 mM potassium hydrogen phthalate (pH 5.6) or 50 mM sodium borate (pH 8.5) buffer was used. A Varian 400 spectrometer equipped with an ATB8123-400 autoswitchable probe tuned to ^{19}F (376.14 MHz) was used. Reaction solutions were composed of 600 μL of buffer solution and 200 μL of D_2O in a 5-mm NMR tube. Immediately prior to sample insertion, 20 μL of PFMP was added to the NMR tube followed by inversion. Reaction kinetics were followed by acquiring NMR spectra using a preacquisition delay program such that one complete spectrum was obtained every 20−30 min. Each spectrum consisted of 12 scans with an acquisition time of 1 s. To ensure quantitive results, a standard of PFPrA under the same reaction conditions as PFMP hydrolysis was subject to a pulse inversion−recovery T_1 relaxation experiment to determine a suitable relaxation delay time for PFMP. In this case, a delay time of 20 s for PFMP was chosen. After acquisition, data analysis was performed using the VnmrJ software (Agilent Technologies) as it possesses a built-in kinetic analysis module. Each arrayed spectrum was Fourier transformed with a line broadening apodization of 6 Hz to improve its signal-to-noise ratio. Kinetic data were obtained by fitting an exponential growth or decay function to the fluorinated signals in the NMR spectra (see Figure S5, Supporting Information). All hydrolysis experiments were performed at 25 °C.

Computational Method. Calculations to determine the significance of PFMP hydration were performed using the *Gaussian 03* program[16] with the WebMO interface. All computations were performed using Density Functional Theory (DFT) with B3LYP functionals using the 6-311G(d,p) basis set. Computations were carried out for both the gas phase and the aqueous phase using a polarizable continuum solvent model (PCM).[17] Equilibrium constants for hydration were computed using the relative method of Gomez-Bombarelli et al.[18] and using a training set calibration of fluoroacetone, trifluoroacetone, and hexafluoroacetone (see SI for details).

Reagents. All chemicals were used as received. PFMP was purchased from Synquest Laboratories (Alachua, FL). Disodium tetraborate and potassium hydrogen phthalate were purchased from BDH (Toronto, ON). Trifluoroacetic acid and heptafluoropropionic acid (PFPrA) were purchased from Sigma-Aldrich (Oakville, ON).

Table 1. Kinetic Data for PFMP Degradation via Photolysis and Hydrolysis ($N = 2$) at Two Different pH Values (For Complete Photolysis Data, Refer to the SI)

mechanism	conditions	rate constant k (s^{-1})	lifetime τ (hours)
photolysis	45° N June 21	3.5×10^{-6a}	79.4
photolysis	45° N December 21	5.9×10^{-7a}	471
photolysis	45° N March 21/Sept 21	2.1×10^{-6a}	132
hydrolysis	pH 5.6	$1.9 \times 10^{-4} \pm 1 \times 10^{-5b}$	1.5 ± 0.1
hydrolysis	pH 8.5	$3.1\times 10^{-4} \pm 3 \times 10^{-5b}$	0.9 ± 0.1

[a] Averaged 24 h rate constant. [b] Pseudo-first-order rate constant.

RESULTS AND DISCUSSION

Photolysis Kinetics. Photolysis lifetimes of PFMP have been determined experimentally in two studies, yielding lifetimes of approximately 1−2 weeks[10] and 1 week.[11] Using the flux conditions and quantum yield (0.043) previously described,[11] and the UV spectrum measured in this study (see SI), photolysis rates for PFMP were estimated. The photolysis rates, presented in Table 1, agree to within a factor of 2 with those reported in previous studies as well as previous measurements of the UV spectrum.[10,11] The 24-h averaged rate constants for photolysis of PFMP for different latitudes are given in the SI. Annual averaged photolytic rate constants (J) ranged from 3.1×10^{-6} to 8.2×10^{-7} s^{-1} corresponding to lifetimes of 4−14 days depending on latitude and time of year.

Photolytic Production of PFCAs under Low NO_x Conditions. Offline samples were taken to determine if photolytic degradation of PFMP could yield PFCAs. The formation of PFCAs in the chamber is only expected under low-NO_x conditions in the presence of HO_2 radicals. Material was not added specifically for the purpose of forming HO_2 radicals, but it is likely that HO_2 radicals are present in small quantities in all chamber experiments because of hydrocarbon residue on the walls of the chamber (the chamber has been used at Ford for many years to study hydrocarbon oxidation mechanisms). Large initial concentrations of PFMP (520 mTorr) were used in the smog chamber to facilitate detection of small yields of PFCAs.

Photolysis of PFMP can generate two different perfluoroacyl radicals:

$$CF_3CF_2C(O)CF(CF_3)_2 + h\nu \rightarrow CF_3CF_2\cdot + \cdot C(O)CF(CF_3)_2 \tag{1}$$

$$CF_3CF_2C(O)CF(CF_3)_2 + h\nu \rightarrow CF_3CF_2C\cdot(O) + \cdot CF(CF_3)_2 \tag{2}$$

Perfluoroacyl radicals either decompose via elimination of CO or add O_2 to give perfluoroacyl peroxy radicals. In low-NO_x environments, perfluoroacyl peroxy radicals can react with HO_2 to give PFCAs:[12]

$$CF_3(CF_2)_xC\cdot(O) + O_2 \rightarrow CF_3(CF_2)_xC(O)OO\cdot \tag{3}$$

$$CF_3(CF_2)_xC(O)OO\cdot + HO_2 \rightarrow CF_3(CF_2)_xC(O)OH + O_3 \tag{4}$$

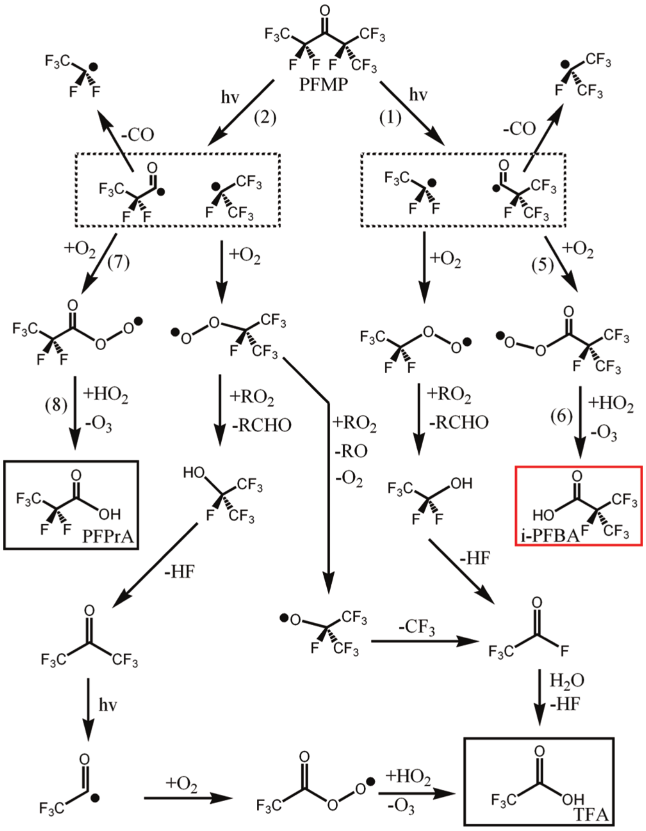


Figure 1. Proposed mechanistic pathways leading to the formation of PFCAs after photolysis of PFMP in the absence of NO_x. Reaction numbers from the text are given in parentheses. Compounds in black boxes represent stable degradation products observed experimentally. Compounds in red boxes represent stable degradation products that were predicted but not observed.

The perfluoroacyl radicals derived from the photolysis of PFMP can react to give *i*-PFBA or PFPrA as follows:

$$(CF_3)_2CFC\cdot(O) + O_2 \rightarrow (CF_3)_2CFC(O)OO\cdot \tag{5}$$

$$(CF_3)_2CFC(O)OO\cdot + HO_2 \rightarrow (CF_3)_2CFC(O)OH\ (i\text{-PFBA}) + O_3 \tag{6}$$

$$CF_3CF_2C\cdot(O) + O_2 \rightarrow CF_3CF_2C(O)OO\cdot \tag{7}$$

$$CF_3CF_2C(O)OO\cdot + HO_2 \rightarrow CF_3CF_2C(O)OH\ (\text{PFPrA}) + O_3 \tag{8}$$

PFPrA was observed in offline samples taken after 45 min of irradiation, at a concentration of 0.061 mTorr. *i*-PFBA was not detected in any of the samples.

The high concentrations of PFMP used in the experiments saturated the FTIR signal and a direct determination of the amount of PFMP photolyzed was not possible. The amount of PFMP lost via photolysis was estimated from the photolysis half-life (determined to be 26 h by the observed formation of $CF_3C(O)F$ as discussed previously[10]) in the chamber conditions. We estimate that 10.4 mTorr of PFMP was photolyzed after 45 min and hence the yield of PFPrA is 0.6%. The low PFPrA yield observed in this experiment probably reflects the low level of

HO_2 radicals available in the system. Sulbaek Andersen et al.[19] reported that the yield of PFPrA from $CF_3CF_2C{\cdot}(O)$ via reactions 7 and 8 was 24 ± 4%. Similarly, the yield of *n*-PFBA in reactions analogous to 5 and 6 was shown to be 10 ± 2%.[12] We expect the yield of *i*-PFBA following formation of $(CF_3)_2CFC{\cdot}(O)$ radicals in an excess of HO_2 radicals to be similar to that reported for *n*-PFBA. The low yield of PFPrA observed in the present experiments suggests either that the yield of $CF_3CF_2C{\cdot}(O)$ radicals in the photolysis of PFMP is low, or that the concentration of HO_2 radicals in the channel is low and conversion of $CF_3CF_2C{\cdot}(O)$ radicals into PFPrA is inefficient. The absence of any discernible formation of *i*-PFBA suggests the latter explanation is more probable. Figure 1 illustrates some mechanistic pathways leading to PFCAs following photolysis of PFMP in the absence of NO_x. Note, as indicated in Figure 1, decomposition via elimination of CO is a significant fate of $CF_3CF_2C{\cdot}(O)$ radicals.[13]

The presence of PFPrA and the absence of *i*-PFBA suggests reaction 2 is favored over reaction 1. This observation was surprising given the perfluoroisopropyl radical is less stable than the perfluoroethyl radical. In the perfluoroethyl radical, two fluorine atoms are able to donate electron density from their lone pair orbitals into the singly occupied p orbital on the radical center, resulting in stabilization. Because the experimental results suggest this is happening, it is proposed that the stabilities of the corresponding perfluoroacyl radicals must allow this observed regioselectivity to occur.

Hydrolysis Kinetics. The hydrolysis reaction of PFMP can proceed by the well-known Haloform reaction mechanism in which a ketone with a suitable alkyl leaving group reacts with water to form a carboxylate and an alkane.

In a typical Haloform reaction, a methyl ketone is tri-iodinated followed by treatment with base to produce a carboxylic acid and iodoform which precipitates as a yellow solid. This reaction is the classic qualitative test for a methyl ketone. The following steps mechanistically describe the Haloform reaction:

$$RC(O)CX_3 + OH^- \rightarrow RC(O^-)(OH)CX_3 \qquad (9)$$

$$RC(O^-)(OH)CX_3 \rightarrow RC(O)(OH) + CX_3^- \qquad (10)$$

$$RC(O)(OH) + CX_3^- \rightarrow RC(O)(O^-) + CHX_3 \qquad (11)$$

where X = Cl/Br/I.

The final step in the Haloform reaction is a rapid and exothermic proton transfer from the carboxylic acid to the carbanion which makes the whole process irreversible. The overall mechanism of the reaction is $B_{AC}2$ which consists of separate addition and elimination steps via a tetrahedral intermediate. The rate determining step is reaction 9. The final two products expected from PFMP hydrolysis are PFPrA and HFC-227ea. The mechanism for hydrolysis of PFMP is shown in Figure 2.

The hydrolysis of PFMP and the detection of both products has been reported by Saloutina et al.[20] however this study was performed at pH values much higher than those relevant for the environment. The objective of the present study was to investigate whether PFMP could undergo hydrolysis at pH values more typical of those found in the environment. The two pH values chosen were 5.6 and 8.5 because pH 5.6 is typical of atmospheric water.[21] A pH of 8.5 was also chosen to represent the upper environmental limit where hydrolysis would likely be the fastest since the Haloform reaction is base catalyzed.

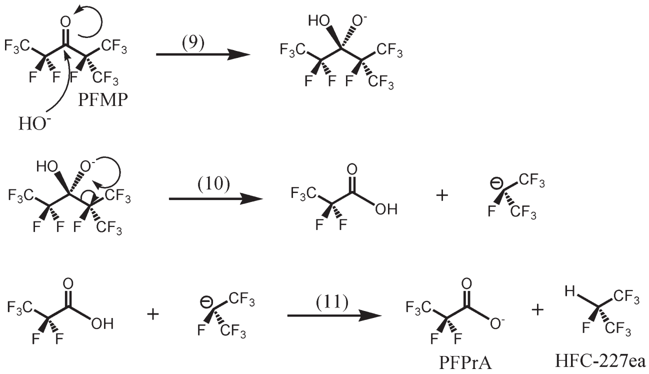


Figure 2. Hydrolysis mechanism of PFMP to produce PFPrA and HFC-227ea under mildly basic conditions. Reaction numbers in the text are given in parentheses.

To measure the kinetics of PFMP degradation, an analytical method to quantify PFMP is required. Liquid chromatography is not suitable to analyze PFMP because authentic standards would rapidly degrade in any protic solvent. It was confirmed in a separate study (data not shown) that PFMP reacts rapidly with methanol to produce HFC-227ea and the methyl ester of PFPrA. PFMP is certainly volatile enough to be analyzed by gas chromatography—mass spectrometry. However aqueous samples would need to be extracted into a suitable GC solvent prior to injection. PFMP was found to have very low solubilities in almost every solvent tested. In addition, such a procedure would require a separate extraction for every time point, greatly increasing the amount of material needed. We decided that ^{19}F NMR would offer the best capability for measuring the kinetics of PFMP in situ. The hydrolysis reaction was performed in an NMR tube and scans of the reaction mixture were taken at various time intervals for subsequent analysis. ^{19}F NMR offers acceptable signal-to-noise ratios and since neither water nor the buffers used contain fluorine atoms, a purely deuterated solvent does not need to be used. For NMR data to be considered quantitative to 99+% accuracy, it is necessary that the relaxation delay between scans be five times that of the longest spin—lattice relaxation time (T_1) in the compound of interest. Because T_1 values can depend on the solvent used, a standard of PFPrA in the aqueous buffer of interest was used as a surrogate for the T_1 of PFMP. It was found that the longest observed T_1 (PFPrA) = 4.0 s, thus making a suitable relaxation delay for PFMP to be 20 s.

The current Varian NMR processing software, VnmrJ, is capable of analyzing kinetic data using a nonlinear fitting algorithm, provided the fit is exponential. Because the concentration of both OH^- and water are constant in each experiment, pseudo-first-order conditions with respect to PFMP were achieved and an exponential decrease in [PFMP] is expected due to hydrolysis. After fitting the data points, the software provides the 1/e lifetime of the compound (τ), which is simply the reciprocal of the pseudo-first-order rate constant, k_{obs}.

The ^{19}F NMR spectrum of PFMP consists of four peaks: each a multiplet due to the long-range J coupling observed for fluorine atoms. The spectra of PFPrA and HFC-227ea combined resemble that of PFMP but the chemical shifts are distinct and the coupling patterns are very different. Thus, it is straightforward to distinguish PFMP from its degradation products. For examples of ^{19}F NMR spectra of both PFMP and its photolysis products, please see the SI.

In summary, we observed the 1/e lifetime of PFMP hydrolysis to vary depending on the pH of the buffer used. The reaction was faster in more alkaline solutions as shown in Table 1. This is entirely reasonable given the base-catalyzed nature of the reaction. Both PFPrA and HFC-227ea were positively identified as the sole products of the hydrolysis reaction. PFPrA was confirmed by comparison to an authentic standard. HFC-227ea was confirmed by comparison to a literature spectrum.[22]

Saloutina et al.[20] did not report any kinetics in their study on the hydrolysis of PFMP, however it is not surprising they observed high yields in PFPrA and HFC-227ea given the strongly basic conditions of their reaction solutions. A further study by the same group[23] elaborated on the specificity of the C−C bond cleavage step to exclusively produce the more stable carbanion leaving group. In the case of perfluorinated compounds, the more substituted anion is more stable because of increased hyperconjugation from the anion lone pair to the vicinal antibonding C−F orbitals. Sykes et al.[24] confirmed the regioselectivity of the Haloform reaction for a number of polyfluorinated ketones. Hence, there is precedent for the Haloform reaction to occur regioselectively in fluorinated ketones to produce the less substituted carboxylate and the more substituted hydrofluoroalkane.

Hydration of PFMP. Aldehydes and ketones can react with water to produce a geminal diol by the following reaction scheme.

$$\mathrm{RC(O)R' + H_2O \rightarrow RC(OH)(OH)R'} \qquad (12)$$

The reaction is catalyzed by both acids and bases and is usually a reversible equilibrium reaction. For most aldehydes and ketones, the equilibrium constant, K_{hyd}, usually strongly favors the carbonyl compound due to the high strength of the C═O bond. Exceptionally, formaldehyde (HC(O)H) exists in aqueous solution purely as the gem-diol (HC(OH)(OH)H) due to its high K_{hyd} value ($\log K_{\text{hyd}} = 3.36$).[25] The vast majority of ketones are quite unreactive to hydration (acetone has $\log K_{\text{hyd}} = -2.85$[25]) and the geminal diol form is usually neglected in reaction schemes. Other exceptions can be halogenated ketones; trichloroacetaldehyde has a $\log K_{\text{hyd}} = 4.45$ and hexafluoroacetone (HFA) has $\log K_{\text{hyd}} = 6.08$.[25] Effectively, there is quantitative conversion of the carbonyl to the hydrate in aqueous solution and the reverse reaction back to the carbonyl does not occur appreciably at room temperature. For example, HFA is provided commercially as the geminal diol derivative.

It might be reasonable to assume that the electron withdrawing groups of HFA impart a strong partial positive charge at the fluorinated carbonyl carbon, resulting in enhanced electrophilicity and hence, a greater degree of hydration. However, Linderman et al.[26] used Hartree−Fock computational methods and found most of the positive electric potential in HFA is found on the CF_3 carbons and not the carbonyl carbon. Instead, they propose the lower energy level of the LUMO of fluorinated ketones compared to their hydrogenated analogs is the major cause of the enhanced reactivity toward water. Because PFMP is perfluorinated like HFA, it would be a reasonable assumption that PFMP could rapidly and irreversibly form a geminal diol in the environment. The PFMP hydrate would not absorb actinic radiation due to the absence of the C═O chromophore. In addition, formation of the diol would increase water solubility and decrease vapor pressure, resulting in a greater rate of wet deposition and enhancing the potential role of hydrolysis. Thus, it is important to determine whether PFMP could form a stable hydrate in the same manner as HFA.

The hydration reaction of PFMP was investigated in our laboratory and no evidence of such a hydrated species was observed (data not shown). This was puzzling as other fluorinated ketones are known to hydrate readily.[25] To provide further insight, computational methods were used to estimate K_{hyd} for PFMP and compare it to other fluorinated carbonyls using the methods of Gomez-Bombarelli et al.[18] The effects of including an aqueous PCM solvent model were also studied although Guthrie et al.[27] previously noted difficulties of applying the PCM model to halogenated compounds. For full details on the computational work, please see the SI.

Depending on the method used to calculate K_{hyd} (see SI), different values for PFMP were obtained ($-2.09 < \log K_{\text{hyd}} < -0.43$) but the range suggests hydrate formation is not significant for PFMP. Given the perfluorinated nature of PFMP and that even partially fluorinated ketones such as trifluoroacetone ($\log K_{\text{hyd}} = 1.54$)[25] have large K_{hyd} values we were surprised by the low values of K_{hyd} calculated for PFMP. The computational methods used in the present study (B3LYP/6-311++G(d,p)) were able to compute K_{hyd} values for several fluorinated ketones (fluoroacetone, trifluoroacetone, and hexafluoroacetone) with fairly good accuracy, providing confidence in the method used. A single point molecular orbital calculation on geometry-optimized PFMP in the gas phase (B3LYP/6-311++G(d,p)) gave the energy level of the LUMO (−84.1 kcal/mol) as almost identical to the LUMO of HFA (−81.4 kcal/mol), especially when compared to the computed LUMO of acetone (−19.3 kcal/mol). This supports the results of Linderman et al.[26] who proposed these energy differences as the reason for the enhanced reactivity of HFA to hydration. In the case of PFMP, steric hindrance could be the reason for its decreased hydration equilibrium constant compared to HFA. We conclude that geminal diol formation is not a significant environmental fate for PFMP.

ENVIRONMENTAL IMPLICATIONS

We have investigated the potential for photolysis, hydrolysis, and hydration to contribute to the environmental fate of PFMP. As discussed in the previous section, hydration is not a significant fate for PFMP. While the rate constant for hydrolysis is much greater than that for photolysis, the levels of liquid water in the atmosphere are usually very low. A typical cloud only contains approximately 3×10^{-7} cm^3 liquid water per mL of total volume[28] and we conclude that even at night, the amount of PFPrA and HFC-227ea produced would not be significant and that photolysis dominates hydrolysis as the atmospheric fate of PFMP. Cahill and Mackay[29] came to the same conclusion in their modeling study. Interestingly, Cahill and Mackay predicted a hydrolysis rate constant at pH 5.6 of 2.2 s^{-1} which is approximately 10^4 times larger than the hydrolysis rate constant we measured. Hence, our work suggests hydrolysis is an even less important fate for PFMP compared to photolysis than the ratio Cahill and Mackay[29] predicted; the ratio of rates of photolysis to hydrolysis is approximately 980,000,000:1. For full details on this calculation, please see the SI. Photolysis will always dominate over hydrolysis. It is clear the very low fraction of liquid water in the atmosphere contributes heavily to this ratio and more than offsets the higher hydrolysis rate constant. This ratio is so great that even at night time during a heavy rain event it is unlikely hydrolysis will occur to any significant extent.

Photolysis is the dominant mechanism by which PFMP is removed from the atmosphere. It has been established previously[10,11] that photolysis of PFMP in the presence and absence of NO_x will lead to the formation of $CF_3C(O)F$ in a molar yield of approximately 100%. The atmospheric fate of $CF_3C(O)F$ is hydrolysis to give trifluoroacetic acid (TFA). TFA is a ubiquitous naturally occurring component of the hydrosphere and the additional burden associated with PFMP photolysis is not significant. In the present work, we also show that small amounts of PFPrA are also formed as a result of PFMP photolysis. To provide a crude upper limit estimate for the amount of PFPrA that might be expected in precipitation as a result of atmospheric degradation of PFMP we applied the following logic (see SI for details). The production of PFMP by 3 M is 100−1000 t $year^{-1}$ and began in approximately 2003.[30] Given PFMP is used entirely in fire-protection systems that are released by an alarm, it can be considered stored emission potential with releases averaging 1−3% $year^{-1}$.[30] Combining the upper limit of production (1000 t $year^{-1}$) with a 3% emission factor provides an upper limit of 30 t of PFMP released into the atmosphere each year. Reactions subsequent to the formation of $CF_3CF_2C(O)$ radicals in air in the presence of excess HO_2 give PFPrA in a molar yield of 24%.[12] Using a simple model (see SI), and assuming the photolysis of PFMP proceeds exclusively via reaction 2, we derive an upper limit of 0.6 ng L^{-1} for the average concentration of PFPrA in precipitation resulting from PFMP oxidation. Perfluoropropionic acid has been detected in rainwater at several sites in North America at concentrations on the order of 1−10 ng L^{-1} and these levels have yet to be explained.[3] The photolysis of PFMP contributes to, but does not appear to be the major source of, PFPrA observed in precipitation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** All computational experiment methodologies, photolysis rate constants from the TUV model, full modeling calculations on the environment fate of PFMP, ^{19}F NMR spectra, and the UV−vis spectrum of PFMP. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: [redacted]; e-mail: [redacted]@chem.utoronto.ca.

■ ACKNOWLEDGMENT

We thank Prof. Mark Taylor and Dr. Mima Staikova for assistance in the computational modelling. Funding to D.A.J. was provided through an Ontario Graduate Scholarship. Funding to C.J.Y. was provided by an NSERC Canada Graduate Scholarship.

■ REFERENCES

(1) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. Biological monitoring of polyfluoroalkyl substances: a review. *Environ. Sci. Technol.* **2006**, *40*, 3463–3473.

(2) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Petrick, G.; Gamo, T. A global survey of perfluorinated acids in oceans. *Mar. Pollut. Bull.* **2005**, *51*, 658–668.

(3) Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. Poly and perfluorinated carboxylates in North American precipitation. *Environ. Sci. Technol.* **2006**, *40*, 7167–7174.

(4) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2003**, *22*, 196–204.

(5) Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. *Nature* **2001**, *412*, 321–324.

(6) Key, B. D.; Howell, R. D.; Criddle, C. S. Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **1997**, *31*, 2445–2454.

(7) Tang, X.; Madronich, S.; Wallington, T. J.; Calamari, D. Changes in tropospheric composition and air quality. *J. Photochem. Photobiol. B* **1998**, *46*, 83–95.

(8) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38*, 3316–3321.

(9) Young, C. J.; Mabury, S. A. Atmospheric perfluorinated acid percursors: chemistry, occurrence and impacts. *Rev. Environ. Contam. Toxicol.* **2010**, *208*, 1–110.

(10) Taniguchi, N.; Wallington, T. J.; Hurley, M. D.; Guschin, A. G.; Molina, L. T.; Molina, M. J. Atmospheric chemistry of $C_2F_5(O)CF(CF_3)_2$: Photolysis and reaction with Cl atoms, OH radicals and ozone. *J. Phys. Chem. A* **2003**, *107*, 2674–2679.

(11) D'Anna, B.; Sellevag, S. R.; Wirtz, K.; Nielsen, C. J. Photolysis study of perfluoro-2-methyl-3-pentanone under natural sunlight conditions. *Environ. Sci. Technol.* **2005**, *39*, 8708–8711.

(12) Sulbaek Andersen, M. P.; Stenby, C.; Nielsen, C. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. Atmospheric chemistry of $n\text{-}C_xF_{2x+1}CHO$ (x = 1,3,4): Mechanism of the $C_xF_{2x+1}C(O)O_2 + HO_2$ reaction. *J. Phys. Chem. A* **2004**, *108*, 6325–6330.

(13) Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Sulbaek Andersen, M. P.; Nielsen, O. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. Atmospheric chemistry of $n\text{-}C_xF_{2x+1}CHO$ (x = 1,3,4): Fate of $n\text{-}C_xF_{2x+1}C(O)$ radicals. *J. Phys. Chem. A.* **2006**, *110*, 12443–12447.

(14) Fuson, R. C.; Bull, B. A. The Haloform reaction. *Chem. Rev.* **1934**, *15*, 275–309.

(15) Madronich, S.; Flocke, S. In *Handbook of Environmental Chemistry*; Boule, P., Ed.; Springer: Heidelberg, 1998.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Wallingford, CT, 2003.

(17) Miertus, S.; Scrocco, E.; Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects. *Chem. Phys.* **1981**, *55*, 117–129.

(18) Gomez-Bombarelli, R.; Gonzalez-Perez, M.; Perez-Prior, M. T.; Calle, E.; Casado, J. Computational calculation of equilibrium constants: Addition to carbonyl compounds. *J. Phys. Chem. A* **2009**, *113*, 11423–11428.

(19) Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Nielsen, C. J. Atmospheric chemistry of C_2F_5CHO: Reaction with Cl atoms and OH radicals, IR spectrum of $C_2F_5C(O)O_2NO_2$. *Chem. Phys. Lett.* **2003**, *379*, 28–36.

(20) Saloutina, L. V.; Filyakova, T. I.; Zapevalov, A. Y.; Kodess, M. I.; Kolenko, I. P. Synthesis and some reactions of 2-X-perfluoro-2-methyl-3-pentanones. *Russ. Chem. Bull.* **1982**, *8*, 1893–1896.

(21) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, CA, 2000.

(22) Foris, A. ^{19}F and ^{1}H NMR spectra of halocarbons. *Magn. Reson. Chem.* **2004**, *42*, 534–555.

(23) Saloutina, L. V.; Zapevalov, A. Y.; Kodess, M. I.; Kolenko, I. P.; German, L. S. Perfluoro- and Polychloroketones in the Haloform cleavage reaction. *Russ. Chem. Bull.* **1983**, *5*, 1114–1116.

(24) Sykes, A.; Tatlow, J. C.; Thomas, C. R. A new synthesis of fluoro-ketones. *J. Chem. Soc.* **1956**, 835–839.

(25) Guthrie, J. P. Carbonyl addition reactions: Factors affecting the hydrate-hemiacetal and hemiacetal-acetal equilibrium constants. *Can. J. Chem.* **1975**, *53*, 898–906.

(26) Linderman, R. J.; Jamois, E. A. A semi-empirical and ab-initio analysis of fluoroketones as reactive electrophiles. *J. Fluorine Chem.* **1991**, *53*, 79–91.

(27) Guthrie, J. P.; Povar, I. *Can. J. Chem.* **2009**, *87*, 1154.

(28) De Bruyn, W. J.; Shorter, J. A.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Uptake of haloacetyl and carbonyl halides by water surfaces. *Environ. Sci. Technol.* **1995**, *29*, 1179–1185.

(29) Cahill, T.; Mackay, D. Assessment of the atmospheric fate of Novec 1230. A report prepared for 3M in support of the registration of Novec 1230 in Canada; Canadian Environmental Modelling Centre, Trent University: Peterborough, ON, 2002.

(30) Werner, K. Production of PFMP by 3M Company (personal correspondence).