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# Atmospheric fate of 4:2 fluorotelomer alcohol using an oxidation flow reactor and proton transfer reaction time-of-flight mass spectrometry

Alessia A. Colussi, <sup>a</sup> Trevor C. VandenBoer, <sup>a</sup> Cora J. Young <sup>\*a</sup> and John Liggi<sup>\*b</sup>

Commonly used methodologies applied to studying the atmospheric degradation of per- and polyfluoroalkyl substances (PFAS) require analyses to be conducted offline and under dry conditions, potentially limiting the atmospheric relevance of the resulting mechanism and kinetics. We coupled an oxidation flow reactor (OFR) to a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS), focusing on the NO<sub>x</sub>-free oxidation of a perfluorocarboxylic acid precursor – the 4:2 fluorotelomer alcohol (FTOH) – in the first application of this system to PFAS. The PTR-ToF-MS was calibrated under dry conditions (0 to 1% RH) and at relative humidities (RHs) of 22%, 44%, and 60%. The oxidation of 4:2 FTOH by <sup>•</sup>OH radicals was observed in real-time, as a function of RH, with PTR-ToF-MS detecting both primary and secondary 4:2 FTOH degradation products: the 4:2 fluorotelomer aldehyde and 4:2 fluorotelomer carboxylic acid, respectively. The resulting pseudo-first-order kinetics (*k*<sub>obs</sub>) were determined and compared to previously reported FTOH values. The determined *k*<sub>obs</sub> values were (1.0 ± 0.1) × 10<sup>-12</sup> (22% RH), (7.4 ± 0.8) × 10<sup>-13</sup> (44% RH), and (7.2 ± 0.8) × 10<sup>-13</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> (60% RH), comparable to prior reports at 22% RH and lower as RH increased. This type of experiment demonstrates that the OFR-PTR-ToF-MS technique can be transferred to study other suspected, but uncharacterized, atmospheric PFAS transformations.

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## Environmental significance

Volatile per- and polyfluoroalkyl substances (PFAS), such as fluorotelomer alcohols (FTOHs), can be emitted into the atmosphere from industrial and commercial sources. Their degradation leads to the formation of persistent perfluorocarboxylic acids, detected globally in urban, rural, and 5 remote regions. Previous studies on FTOH oxidation were conducted under dry conditions, limiting their atmospheric relevance. Here, we investigate the OH oxidation of 4:2 FTOH under 7 NO<sub>x</sub>-free and humid conditions using an oxidation flow reactor coupled to proton transfer reaction time-of-flight mass spectrometry. We observed decreasing reaction rates with increasing humidity, highlighting the need to consider water vapour in FTOH chamber experiments and models. This work provides more representative kinetics for atmospheric models, supporting improved understanding of PFAS transport and environmental fate.

## 1 Introduction

For over seven decades, a diverse group of synthetic, fluorinated organic compounds known as per- and polyfluoroalkyl substances (PFAS) have been widely used for industrial and commercial applications. Due to the strength and stability of the carbon–fluorine bond, PFAS have ideal chemical properties, such as hydrophobicity and lipophobicity, and are utilized in various applications (*e.g.*, food packaging, textiles, electroplating of metals).<sup>1</sup> They can enter the atmosphere directly *via* emissions from manufacturing facilities, wastewater treatment

plants, landfills, *etc.*,<sup>1,2</sup> and their terminal acid degradation products are very resistant to metabolic and environmental degradation.<sup>3</sup> Additionally, some PFAS are considered toxic and bioaccumulative; high levels of PFAS exposure have been associated with adverse health effects in humans<sup>4–7</sup> and wildlife.<sup>8–12</sup>

Volatile and semi-volatile atmospheric PFAS, such as fluorotelomer alcohols (FTOHs), are used in the fluoropolymer and surfactant industry and as chlorofluorocarbon replacements.<sup>13</sup> They are included in the formulations of a variety of products such as adhesives, polishes, paints, and electronic materials<sup>14</sup> and in some cases, the FTOHs can be released directly into the environment from product use.<sup>15</sup> In 2006, the global production of FTOHs was estimated to be between 11 to 14 × 10<sup>6</sup> kg year<sup>-1</sup> with 40% of that production occurring in North America.<sup>16,17</sup> This group of compounds has an estimated atmospheric half-life of 10 to 20 days and are able to be

<sup>a</sup>Department of Chemistry, York University, Toronto, ON, Canada. E-mail: youngcj@yorku.ca

<sup>b</sup>Air Quality Research Division, Environment and Climate Change Canada, Toronto, ON, Canada. E-mail: john.liggi@ec.gc.ca



widespread to achieve relatively uniform hemispheric distribution.<sup>18</sup> Several studies have reported gas-phase FTOHs at tens to hundreds of  $\text{pg m}^{-3}$  in samples from around the world.<sup>19–22</sup> Thus, their atmospheric degradation has been deemed as a plausible contributing source of perfluorocarboxylic acids (PFCAs) found in remote locations such as the Arctic.<sup>23,24</sup>

The atmospheric fate of gas-phase FTOHs has been the subject of several prior investigations, all of which used smog chambers and Fourier transform infrared spectroscopy (FTIR).<sup>16,18,19</sup> More recently, a chamber coupled with mass spectrometry enabled continuous measurements of the degradation products of hydrofluoroether alcohols, a subclass of PFAS, for the first time.<sup>25</sup> Collectively, these smog chamber studies—including the recent work on hydrofluoroether alcohols—were conducted under dry conditions, in part to minimize interference from water vapour. Water is a well-known interferent in smog chamber studies employing methods such as fluorine-19 nuclear magnetic resonance spectroscopy (<sup>19</sup>F NMR),<sup>26</sup> FTIR,<sup>27</sup> and modern mass spectrometry techniques like iodide adduct chemical ionization mass spectrometry (I-CIMS).<sup>28–32</sup> As a result, although the effects of water vapour on the oxidation kinetics of non-fluorinated alcohols (20% to 95% relative humidity, RH)<sup>33–38</sup> have been explored to some extent, comparable data for fluorinated analogues such as FTOHs are lacking. Here we revisit the degradation of 4:2 FTOH under dry and humidified conditions to expand our mechanistic understanding of the atmospheric chemistry of this compound.

In this work, we apply a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) to the study of 4:2 FTOH oxidation by coupling it to an oxidation flow reactor (OFR). This new approach to measuring gas-phase PFAS allows us to examine its atmospheric degradation and formation of products, both facilitated by  $\cdot\text{OH}$  radicals. The use of OFR-PTR-ToF-MS can overcome the experimental limitations of performing oxidation chemistry under more atmospherically relevant RH conditions in the absence of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ). This work shows that: (i) a PTR-ToF-MS can be used to measure gas-phase PFAS, (ii) 4:2 FTOH degradation products can be identified in real-time using PTR-ToF-MS, and (iii) OFR experiments can be used to study the degradation kinetics of 4:2 FTOH and, by extension, many other volatile PFAS.

## 2 Materials and methods

### 2.1 OFR experiments

A custom-built OFR was used in these chamber experiments (Fig. S1) which has been described and characterized previously.<sup>39–41</sup> The current reactor is a fused quartz flow tube with a cone-shaped diffusion inlet and seven outlets. Six of the outlets act as exhaust to reduce gas-phase wall losses and to maintain plug flow.<sup>39</sup> The flow rate through the 16 L OFR was approximately  $2 \text{ L min}^{-1}$ , resulting in a residence time of 8 min. Using the density of air ( $1.293 \text{ kg m}^{-3}$ ) and dynamic viscosity of air ( $1.714 \times 10^{-5} \text{ Pa s}$ ),<sup>42</sup> a Reynolds number of 16 was calculated to confirm laminar flow within the OFR during all experiments. These reactors utilize oxidants at concentrations considerably higher than the ambient atmosphere to accelerate

oxidation chemistry.<sup>43</sup> Within minutes, exposures equivalent to multiple days or weeks of atmospheric oxidation are possible. These higher-than-ambient concentrations are generated by the photolysis of a chosen oxidant precursor using low-pressure ultraviolet (UV) lamps. Compared to traditional smog chambers, the rapid oxidation timeframes result in shorter sample residence times and reduced wall effects within an experiment.<sup>44,45</sup>

Oxidation flow reactors have been used to infer the transition between functionalization (*i.e.*, oxygen addition)<sup>46</sup> and fragmentation (*i.e.*, carbon-carbon bond cleavage)<sup>47</sup> for volatile organic compounds (VOCs), and the subsequent impact of these processes on secondary organic aerosol formation.<sup>40,46,48</sup> It has been noted that these experimental conditions may not fully reflect ambient reaction pathways under all conditions and thus OFRs may have limits on their atmospheric relevance, particularly associated with oxidant formation and alkylperoxy radical ( $\text{RO}_2$ ) chemistry.<sup>43,49,50</sup> The low- $\text{NO}_x$  experiments described in this work follow the standard methodology consistent with OFR best practices; however, one limitation specific to this work is the elevated concentrations of  $\cdot\text{HO}_2$  radicals within the reactor relative to typical atmospheric levels. This increased  $\text{HO}_2$  abundance can alter the radical chemistry by favouring  $\text{RO}_2 + \text{HO}_2$  reactions over  $\text{RO}_2 + \text{NO}$  pathways, which can lead to differences in product distributions. Nonetheless, given that this study does not aim to quantitatively resolve product distributions, the influence of altered radical pathways is not expected to affect the main findings.

Approximately 750 parts-per-billion-by-volume ( $10^{-9} \text{ mol mol}^{-1}$ , ppbv) of externally generated ozone ( $\text{O}_3$ , model TG-10; Ozone Solutions, San Antonio, TX, USA) was introduced into the OFR and was photolyzed using UV light at 254 nm provided by low-pressure mercury lamps (part # 82-3309-9; Jelight Company Inc., Irvine, CA, USA). This produces  $\text{O}(^1\text{D})$ , which reacts with water vapour to generate OH. This method is a well-established approach in OFR studies<sup>43,51–54</sup> and produces a steady-state OH concentration that can be quantitatively estimated using a CO tracer. Radical production is influenced by  $\text{O}_3$  and  $\text{H}_2\text{O}$  concentrations as well as UV lamp intensity, and this configuration is relatively resilient to OH suppression at  $\text{O}_3$  levels reaching up to 70 parts-per-million (ppm) due to a higher OH concentration and enhanced  $\text{HO}_2$  recycling, which helps maintain stable radical chemistry.<sup>53</sup> In the absence of light, we performed negative control experiments of 4:2 FTOH in the presence of residual  $\text{O}_3$  to measure whether any loss took place on the timescales present in this system. The average temperature inside the OFR was  $23.0 \pm 0.7 \text{ }^\circ\text{C}$  and the RHs were controlled at  $21.8 \pm 0.7\%$ ,  $44.0 \pm 3.9\%$ , and  $59.6 \pm 5.5\%$  (model HMP60; Vaisala Oyj, Vantaa, Finland). The OH levels within the OFR were adjusted using the voltages applied to, and the number of, UV lamps. The OH exposure—the product of the average residence time in the reactor and OH concentration—was then estimated by measuring the rate of decay of carbon monoxide (CO)<sup>55</sup> during offline calibrations (Fig. S2). Both CO and  $\text{O}_3$  were measured using standard gas analyzers (CO by model 23r; ABB Inc—Los Gatos Research, San Jose, CA, USA, and  $\text{O}_3$  by model 202; 2B Technologies, Broomfield, CO, USA).



The OH exposure values were determined using the second-order rate constant between CO and OH  $((1.54 \pm 0.14) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1})^{56}$  and the resulting photochemical ages were calculated assuming a global average OH concentration  $(1.50 \times 10^6 \text{ molecules cm}^{-3})^{57}$  (Section S1). The calculated OH exposure ranged from  $1.94 \times 10^{11}$  to  $2.68 \times 10^{12}$  molecules s  $\text{cm}^{-3}$ , and the corresponding photochemical ages at each RH are provided in Table S1.

## 2.2 PTR-ToF-MS measurements

A PTR-ToF-MS (Ionicon Analytik GmbH, Innsbruck, Austria) acquiring data at 0.5 Hz was used to measure the 42 FTOH as it reacted with  $\cdot\text{OH}$  radicals in real-time. The PTR-ToF-MS operating principles and its applications have been described in detail elsewhere.<sup>58–62</sup> Here, the PTR-ToF-MS drift tube pressure was maintained at 2.15 mbar and the electric field at a 600 V difference. The resulting electric field strength ( $E$ ) and buffer gas density ( $N$ ) ratio was 140 Townsend. The mass-to-charge ratio ( $m/z$ ) of the ions are determined by the measured flight times, and an entire mass spectrum ( $m/z \leq 480$ ) is produced with every pulse. Trichlorobenzene (housed in a permeation tube) was continuously added to the inlet to monitor  $m/z$  calibration of the instrument. The raw mass spectra were acquired using TofDaq (Tofwerk AG, Thun, Switzerland) and analyzed using Tofware (Tofwerk AG, Thun, Switzerland). The instrument resolution was approximately 3500  $m/\Delta m$  for the 42 FTOH (exact  $m/z$  265.027492) and high-resolution fitting provided analyte signal intensity based on their exact mass with  $15 \pm 1$  ppm accuracy. Due to RH-dependent  $m/z$  shifts, observed masses for the reagent ion as well as 4:2 FTOH and its degradation products varied slightly across experiments. However, all values remained within the instrument's mass accuracy specification of  $15 \pm 1$  ppm. Therefore, the exact protonated masses were used throughout for analyte identification and reporting.

Calibration was performed by delivering gas-phase 4:2 FTOH (2101-3-95; SynQuest Labs, Alachua, FL, USA) to the PTR-ToF-MS using a custom-made, temperature-controlled permeation device (PD).<sup>63</sup> Approximately 250  $\mu\text{L}$  of 4:2 FTOH was added to a 60 mm perfluoroalkoxy tube (3.2 mm inner diameter with 5 mm outer diameter, part # 5733K73; McMaster-Carr, Aurora, OH, USA) and thermally sealed on both ends, allowing for a consistent mass of 4:2 FTOH gas to permeate at a constant temperature and pressure.<sup>63,64</sup> The PD was housed in an aluminum block that was temperature controlled using a cartridge heater and was regulated to  $75.0 \pm 0.1$  °C, while 10  $\text{mL min}^{-1}$  of dry nitrogen gas flowed over the PD. The mass emission rate was quantified gravimetrically over 26 weeks as  $254 \pm 2$   $\text{ng min}^{-1}$  (Fig. S3). Calibrations covered 3 to 21 ppbv of 42 FTOH and were performed under RH conditions relevant to each experiment, which spanned 22%, 44%, and 60% RH (Section S2 and Fig. S4) using  $m/z$  265.02749. This was required due to the potential for water vapour altering the instrument response. Calibrations were done through the OFR in the absence of light and  $\text{O}_3$ , with mixing ratios controlled by increasing the dilution flow. Zero air passed through a heated platinum catalyst held at 350 °C was used to acquire

a background signal which was then subtracted from each calibration point and normalized to the isotope of the hydrogenium reagent ion ( $\text{H}_3^{18}\text{O}^+$ ,  $m/z$  21.022635) to generate instrument measurements with units of normalized counts per second (ncps).

## 2.3 Data treatment: rate constant, $k_{\text{obs}}$

The rate constant ( $k_{\text{obs}}$ ,  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for  $\cdot\text{OH}$  radicals with 4:2 FTOH was determined by measuring the decrease in FTOH signal as a function of OH exposure (Section S3). Wall loss due to diffusion to the OFR surfaces can lead to lost analyte signal. Using the diffusion coefficient of 1-hexanol as a proxy,<sup>65</sup> the estimated diffusion time across the reactor radius for 42 FTOH molecules was 417 s, slightly shorter than the experimental OFR gas residence time of 468 s. Given the similarity between these two values, the impact of surface effects was examined by fitting the system response times to single and double exponential functions during the calibration (Table S2) and  $k_{\text{obs}}$  determinations (Table S3) at each RH (see Section 3.2).

# 3 Results and discussion

## 3.1 PTR-ToF-MS: technique for measuring gas-phase PFAS

There are few reports considering the applicability or limitations of using atmospheric mass spectrometry techniques for the detection of volatile PFAS in ambient air compared to controlled lab conditions. Here, the sensitivity and two-second limit of detection (LOD, assuming a signal-to-noise ratio of 3) for 4:2 FTOH under dry conditions were  $(12.7 \pm 0.6) \times 10^{-3}$  ncps ppbv $^{-1}$  and 63 parts-per-trillion by volume ( $10^{-12}$  mol  $\text{mol}^{-1}$ , pptv), respectively (Section S4 and Table S4). The average sensitivity  $((70.4 \pm 2.3) \times 10^{-4}$  ncps ppbv $^{-1}$ ) and LOD (109 pptv) under humidified conditions was used for the corresponding experiments. Gaseous 42 FTOH has not been previously measured using PTR-ToF-MS and so the sensitivity and LOD values reported here cannot be directly compared to other studies. Rather, we directly compare against that of other common VOCs measured *via* PTR-ToF-MS. The sensitivity value reported here is much smaller than the sensitivity for common VOCs like acetone (30.9 ncps ppbv $^{-1}$ )<sup>66</sup> and ethanol (99.23 ncps ppbv $^{-1}$ ).<sup>67</sup> The lower sensitivity here is reasonable as we would expect FTOHs to have lower proton affinity (PA) than other VOCs due to the electron-withdrawing properties from fluorination. While the PA for 4:2 FTOH has not been reported, that of 1:2 FTOH is 700  $\text{kJ mol}^{-1}$ .<sup>68</sup> The length of the perfluorinated chain has little effect on FTOH properties;<sup>13</sup> hence, it is reasonable to assume the PA of the 4:2 FTOH is  $\sim 700$   $\text{kJ mol}^{-1}$ . This PA is similar to that of water (691  $\text{kJ mol}^{-1}$ )<sup>69</sup> but lower than those of commonly measured VOCs, such as *n*-propanol (786 to 791  $\text{kJ mol}^{-1}$ )<sup>70</sup> and acetone (812  $\text{kJ mol}^{-1}$ ).<sup>71</sup> Our 42 FTOH LOD was also found to be in a comparable range to that reported for acetone using PTR-ToF-MS<sup>72–74</sup> (Table S5), but higher than 4:2 FTOH measured by I-CIMS (7.9 pptv<sup>75</sup> and 2.9 pptv<sup>76</sup>). We note these LODs are orders of magnitude too high to detect ambient FTOHs because average measurements in North America (Table S6), Europe, and Asia have not exceeded 220  $\text{ng m}^{-3}$  (0.022



pptv).<sup>1,16,22,77–79</sup> The Vocus—a PTR-ToF-MS with the highest sensitivity and resolving power on the market—has reported LODs for common VOCs from 10 to 90 pptv<sup>72–74</sup> (Table S5), which suggests even it would be unable to detect ambient FTOHs. Thus, a Vocus, a traditional PTR-ToF-MS, and an I-CIMS are not sufficiently sensitive for the detection of ambient FTOHs, but all are suitable for use in laboratory experiments.

### 3.2 PTR-ToF-MS: real-time detection of 4:2 FTOH degradation products

The experiments carried out in this work focused on the degradation of approximately 10 ppbv of 4:2 FTOH, in the absence of NO<sub>x</sub>, at RHs of 22%, 44%, and 60%. Previous smog chamber studies have only investigated the reactivity of FTOHs, including the 4:2 FTOH, under dry conditions with <sup>•</sup>OH radicals and chlorine (Cl) atoms, in both the presence and absence of NO<sub>x</sub>.<sup>18,80–84</sup> The OH-initiated oxidation pathways of FTOHs were first proposed in 2004 (Fig. 1) and based on smog chamber experiments initiated with Cl atoms, as they react in the same manner with FTOHs as <sup>•</sup>OH radicals.<sup>18</sup> In this initial study, the *in situ* FTIR analysis of FTOH oxidation products suggested the formation of PFCAs at yields below 10%. Due to the low yields and overlapping IR spectra of PFCAs, FTIR lacked the sensitivity and specificity needed for their definitive identification or quantification. Instead, an offline analysis using liquid chromatography tandem mass spectrometry revealed that each FTOH produced a corresponding PFCA retaining the full perfluorinated chain (*i.e.*, 8:2 FTOH produced perfluorononanoic acid). These analyses also showed the formation of a homologous series of shorter-chain PFCAs; for example, the oxidation of 8:2 FTOH resulted in PFCAs ranging from trifluoroacetic acid upward. Additionally, <sup>19</sup>F NMR detected perfluorinated acid fluorides, which can hydrolyze to their corresponding carboxylic acids, thereby providing further evidence for PFCA formation during FTOH atmospheric oxidation. As a result, various studies have since concluded that, in a low NO<sub>x</sub> or NO<sub>x</sub>-free environment, the atmospheric oxidation of FTOHs results in the aldehyde product in a yield close to 100%.<sup>18,23,80,81,85</sup> Thus, the expected first generation oxidation product here was the 4:2 fluorotelomer aldehyde (4:2 FTAL; CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CHO). Further oxidation of 4:2 FTAL has been reported to yield the secondary products 4:2 fluorotelomer carboxylic acid (4:2 FTCA; CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>COOH), 4:2 perfluorinated aldehyde (4:2 PFAL; CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>CHO), and the corresponding peracid (CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>C(O)OOH).<sup>18,81</sup>

During these experiments, the PTR-ToF-MS detected two degradation products – the primary 4:2 FTAL (*m/z* 263.011842) and the secondary 4:2 FTCA (*m/z* 279.006757). No subsequent oxidation products, such as PFCAs (*e.g.*, TFA), were detected under the described experimental conditions. This likely results from limitations of the PTR-ToF-MS being hindered for compounds with strong surface interactions and unfavourable PAs. For example, TFA<sup>69</sup> has a reported PA of 711.7 kJ mol<sup>-1</sup>, which is comparable to that of water<sup>69</sup> and 4:2 FTOH<sup>68</sup> but lower still than those of commonly measured VOCs.<sup>70,71</sup> Additionally, while a secondary product was observed here, further oxidation

to PFCAs is expected based on previous chamber and modelling studies<sup>18,23</sup> but would almost certainly be present below the detection limits of the instrument and require an additional chemical ionization mass spectrometer.<sup>86</sup> Nevertheless, as this study focused on demonstrating the feasibility of real-time PFAS oxidation kinetics and early-stage product identification, Fig. 2 clearly illustrates that as 4:2 FTOH degrades (blue trace), the 4:2 FTAL primary product signal (pink trace) initially increases before it starts to decrease upon reaction to form 4:2 FTCA (purple trace). This trend is also seen at RHs of 44% and 60% (Fig. S5). The 4:2 FTAL primary product can react with OH and photolyze. Available light in the OFR is provided at shorter wavelengths than the most abundant actinic photons, which could affect the observed interconversion rates here. In comparing the cross-sections of the 1:2 and 6:2 FTALs at different wavelengths<sup>85,87</sup> (Table S7), it is possible for photolysis of 4:2 FTAL to occur at 254 nm. However, secondary photolytic product yields within the OFR here are likely underestimated as less photolysis is likely to occur at shorter wavelengths.<sup>85,87</sup> Without calibration standards for the 4:2 FTAL and 4:2 FTCA, we cannot calculate product yields for comparison to previous studies.<sup>87</sup> A third peak of interest was also noted (*m/z* 260.996192; Fig. S5), which we suspect to be the dehydrated form of the 4:2 FTCA. Based on previously reported PTR-MS product-ion fragmentation of non-fluorinated organic acids, the dehydrated 4:2 FTCA may have been formed *via* the loss of water following protonation *via* hydronium.<sup>88</sup> Similar ionization has been previously observed for acetic acid<sup>89</sup> and is believed to result here in an elemental formula of CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>C(O)<sup>+</sup>, with the positive charge on the carbonyl carbon.<sup>88</sup> As with our calibrations for the 4:2 FTOH, the PTR-MS sensitivity towards the detected products decreases with increasing RH.<sup>88–90</sup>

As shown by their widespread global distribution, including to remote regions, some PFAS can undergo long-range atmospheric transport (*i.e.*, neutral, volatile PFAS like FTOHs) or transport *via* global ocean currents (*i.e.*, ionic PFAS).<sup>13,23</sup> With the gas-phase oxidation of FTOHs to PFCAs expected to be more prevalent in remote locations where NO<sub>x</sub> concentrations are low,<sup>18,23</sup> this NO<sub>x</sub>-free work should be more atmospherically representative of such environments. Previous NO<sub>x</sub>-free experiments primarily investigated FTOH reaction mechanisms with Cl atoms. This was done for two main reasons: (i) Cl atoms can be a reliable proxy for <sup>•</sup>OH radicals and (ii) Cl atoms can be more cleanly generated than <sup>•</sup>OH radicals in a Pyrex smog chamber. Where Cl atoms were produced *via* the photolysis of Cl<sub>2</sub>, <sup>•</sup>OH radicals were generated by photolyzing methyl nitrite – generating NO as a byproduct.<sup>91</sup> Other techniques have been used in recent years to cleanly generate <sup>•</sup>OH radicals, such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in an Ingeniven FEP Teflon Gas Sampling Bag to observe hydrofluoroether oxidation.<sup>25</sup> Historically, the photolysis of H<sub>2</sub>O<sub>2</sub> in Pyrex smog chambers fitted with FTIR has been avoided due to the presence of water vapour. These limitations demonstrate the advantages of the described OFR approach here. Since the mechanism of OH oxidation with 4:2 FTOH under NO<sub>x</sub>-free conditions was previously inferred from Cl-initiated experiments, our results ultimately show that



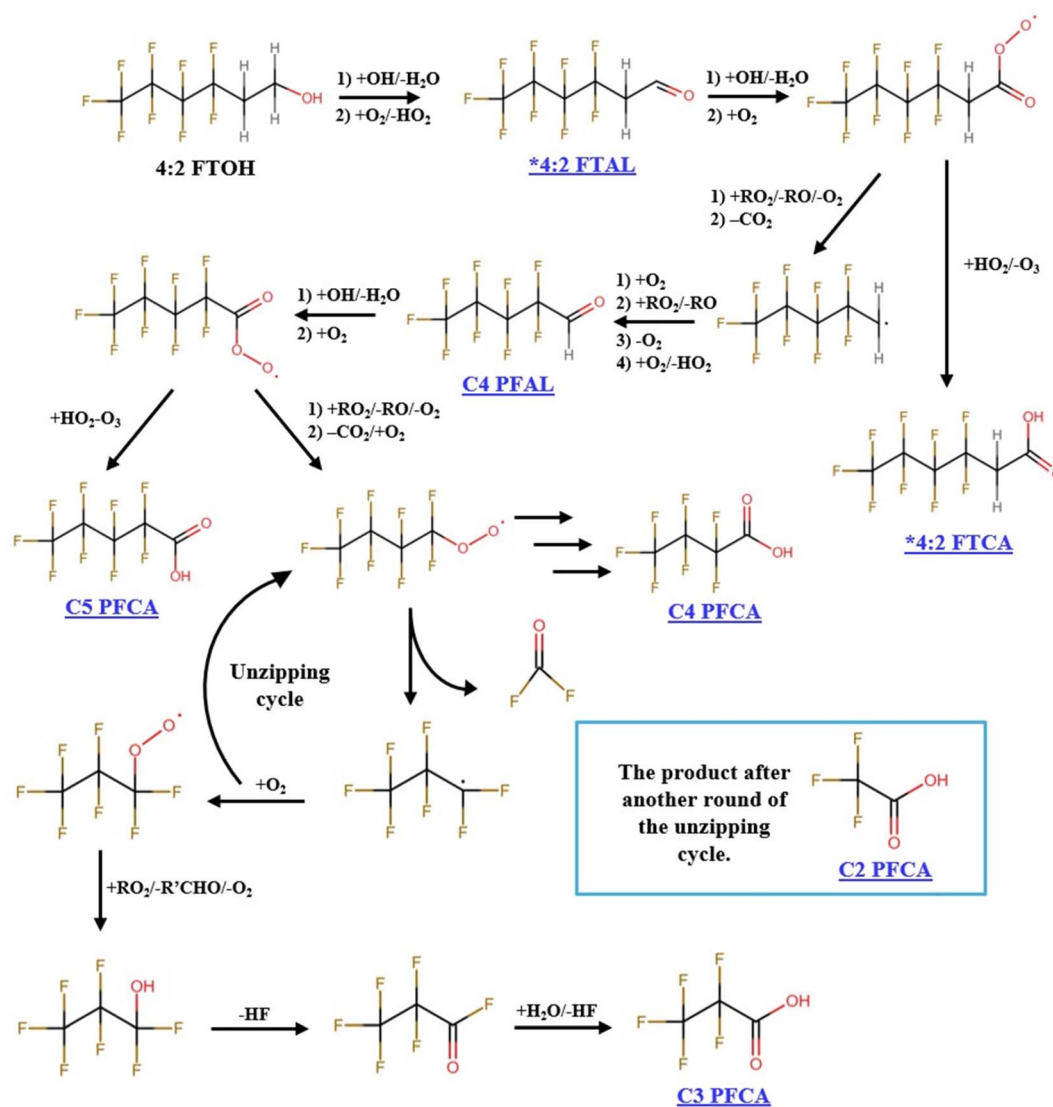


Fig. 1 The proposed atmospheric degradation mechanism of the 4:2 FTOH + <sup>•</sup>OH radicals in a NO<sub>x</sub>-free environment.<sup>18</sup> The expected stable end products are underlined in blue, with the specific products observed in this work being asterisked. The compounds shown are as follows: 4:2 fluorotelomer aldehyde (4:2 FTAL); 4:2 fluorotelomer carboxylic acid (4:2 FTCA); perfluoropentanal (C<sub>4</sub> PFAL); perfluoropentanoic acid (C<sub>5</sub> PFCA); perfluorobutanoic acid (C<sub>4</sub> PFCA); pentafluoropropionic acid (C<sub>3</sub> PFCA); trifluoroacetic acid (C<sub>2</sub> PFCA).

the mechanism under OH-initiated, NO<sub>x</sub>-free conditions is consistent with those predictions.

### 3.3 Oxidation kinetics: OH initiated reaction of 4:2 FTOH

The rate constant for the reactivity of <sup>•</sup>OH radicals with the 4:2 FTOH was determined by measuring the decrease in signal as a function of OH exposure. From the blank-corrected and normalized data, the observed rate constant, *k*<sub>obs</sub> (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), for the oxidation of 4:2 FTOH was determined using eqn (1).<sup>41</sup>

$$\ln \frac{[4:2 \text{ FTOH}]}{[4:2 \text{ FTOH}]_0} = \ln \left( \frac{I}{I_0} \right) = -k_{\text{obs}}[\text{OH}]t \quad (1)$$

Here [4:2 FTOH]<sub>0</sub> is the initial 4:2 FTOH concentration (molecules cm<sup>-3</sup>) and [4:2 FTOH] is the measured 4:2 FTOH concentration (molecules cm<sup>-3</sup>) at a given OH exposure

(molecules s cm<sup>-3</sup>), which is the product of the OH concentration ([OH], molecules cm<sup>-3</sup>) and the average residence time (*t*) in the OFR (s). The *I*<sub>0</sub> and *I* terms are the signal intensities (ncps) for the 4:2 FTOH in the absence and presence of <sup>•</sup>OH radicals, respectively. The reaction is a bimolecular process following a pseudo-first-order reaction, with 4:2 FTOH in excess relative to OH. The value of *k*<sub>obs</sub> was determined by plotting the natural logarithm of the intensity ratios against OH exposure (Fig. 3). At the three different RHs explored here, the *k*<sub>obs</sub> values (Fig. 3a and Table S3) were (1.0 ± 0.1) × 10<sup>-12</sup>, (6.5 ± 0.4) × 10<sup>-13</sup>, and (6.3 ± 0.1) × 10<sup>-13</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 22%, 44%, and 60% RH, respectively. The linear regression coefficients indicate good linearity at all RHs, with *R*<sup>2</sup> ≥ 0.97 (Table S3). Statistical analyses (*t*-test) were performed and the rate constant at 22% RH was significantly different from those at both 44% and 60% RH (*p* < 1 × 10<sup>-6</sup>), whereas no statistically



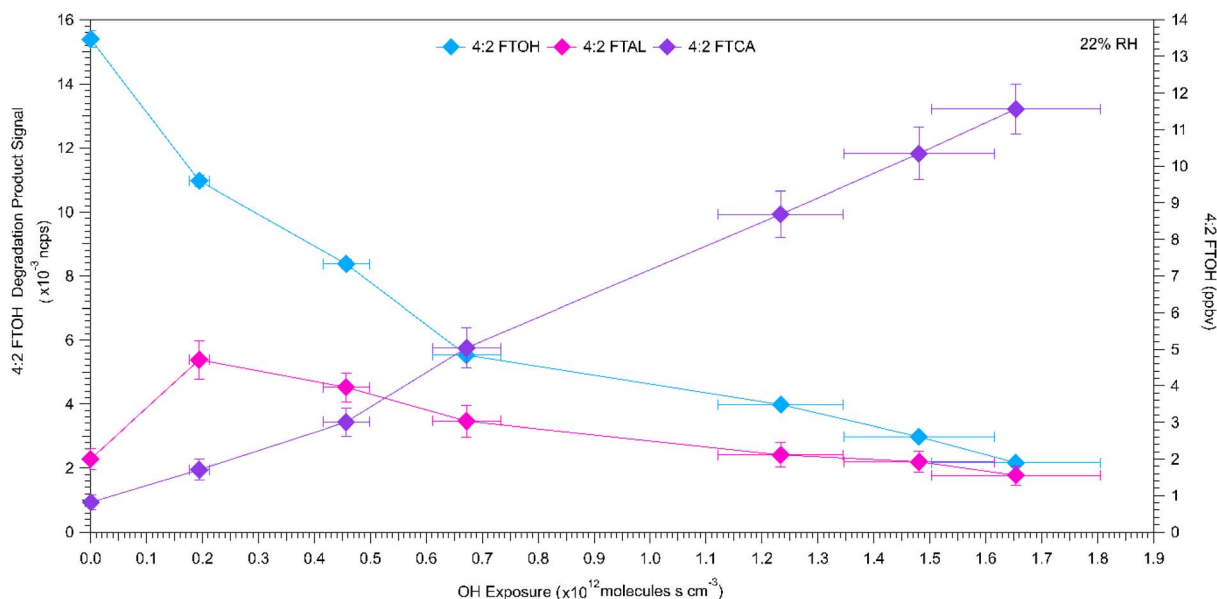


Fig. 2 The change in 4:2 FTOH (ppbv;  $m/z$  265.027492) and the detected degradation products (4:2 FTAL,  $m/z$  263.11842; 4:2 FTCA,  $m/z$  279.006757; ncps) with increasing OH exposure (molecules s  $\text{cm}^{-3}$ ) at 22% RH. The right y-axis depicts the decreasing mixing ratio of permeating 4:2 FTOH, and the propagated error at each point, as it reacts with  $\cdot\text{OH}$  radicals. On the left y-axis are the normalized average signals of the degradation products, with each point's corresponding standard deviation. The x-axis shows the OH exposure and the propagated error at each point.

significant difference was observed between 44% and 60% RH ( $p = 0.26$ ). This suggests that the reaction behaviour changes appreciably between 22% and 44% RH but remains relatively stable at higher humidity levels.

In the only study which reported the OH oxidation rate of 4:2 FTOH in the presence of  $\text{NO}_x$  and under dry conditions, the rate constant was  $(1.07 \pm 0.22) \times 10^{-12}$   $\text{cm}^3$  molecules $^{-1}$  s $^{-1}$ .<sup>80</sup> The  $k_{\text{obs}}$  values measured here are the same order of magnitude. The results are also consistent when compared to kinetic data for the 1:2 and 6:2 FTOHs (Table 1), where chain-length has been found to not affect the kinetics of longer-chained FTOH reactions with OH.<sup>13</sup> It should also be noted that the 4:2 FTOH rate constants measured at 44% and 60% RH are 37% slower (Table S3 and Section S3). Water may induce greater wall effects or altered PTR-MS sensitivity. The 4:2 FTOH could diffuse to the surface of the OFR (417 s) within the experimental residence time (468 s), leading to the potential for wall losses. The instrument response was also calculated at each RH by fitting to single and double exponential functions to account for any changes from surface effects in the OFR and of the PTR-MS sampling inlet. Previously, instrument and inlet surface effects for highly surface active gases (*e.g.*, hydrochloric acid) have been characterized by fitting decay curves to a double exponential.<sup>92–95</sup> Since the 4:2 FTOH is much more volatile and unable to ionize, it is not surprising that system response times were marginally affected resulting in  $k_{\text{obs}}$  that were higher by  $\sim 25\%$  at the two higher RHs when taking these into account with the double exponential approach.

The final average OH reaction rate constant values at 44% and 60% RH are  $(7.4 \pm 0.8) \times 10^{-13}$  and  $(7.2 \pm 0.8) \times 10^{-13}$   $\text{cm}^3$  molecules $^{-1}$  s $^{-1}$ , respectively, when averaging the results obtained from all three calculation approaches (Table 1).

Statistical analyses (*t*-test) were performed and the 'original'  $k_{\text{obs}}$  at 22% RH was found to be significantly different from both averaged  $k_{\text{obs}}$  at 44% and 60% RH ( $p < 1 \times 10^{-4}$ ). However, no statistically significant difference was observed between the averaged rate constants at 44% and 60% RH ( $p = 0.79$ ). Although a statistically significant decrease in the observed rate constants was found between 22% and  $\geq 44\%$  RH, the described experimental setup does not allow us to distinguish between a water vapour dependence of the 4:2 FTOH oxidation and systematic effects associated with increased RH, including diffusion driven wall interactions. While diffusion timescale estimates and exponential fitting analyses suggest that such effects are unlikely to fully account for the observed difference, they cannot be completely ruled out. This suggests that the reaction behaviour differs notably between 22% and 44% RH and increasing it further to 60% RH does not result in statistically significant additional change. Thus, we cannot reliably say that the averaged 44% and 60% RH rate constants are different or that diffusion driven wall interactions are contributing to the slower rates.

Another advantage of using OFR-PTR-ToF-MS in this work is its ability to directly study the decay of 4:2 FTOH with  $\cdot\text{OH}$  radicals. Previously reported chamber experiments have investigated the degradation and reactivity of FTOHs with  $\cdot\text{OH}$  radicals<sup>80,82,83</sup> and Cl atoms<sup>18,81–84</sup> in both the presence and absence of  $\text{NO}_x$ ; however, these experiments were done only under dry conditions. It should first be noted that saturated FTOHs, such as 4:2 FTOH and the structurally related 12 FTOH, do not react appreciably with  $\text{O}_3$  under atmospheric conditions. Negative control experiments performed with  $\text{O}_3$  did not detect any change in FTOH concentration at experimental timescales, consistent with previous findings that reported an atmospheric





Fig. 3 Loss of the 4:2 FTOH following reaction with  $\cdot\text{OH}$  radicals at different OH exposures and RHs. The response time of this method is shown here in the (a) original data as well as after being fitted to (b) single and (c) double exponential functions. The  $k_{\text{obs}}$  values were determined using a linear regression analysis weighted to the error in the y-axis. The  $k_{\text{obs}}$  values for the three different data sets can be found in Table S3.

lifetime of approximately 5900 days for 12 FTOH with respect to reaction with  $\text{O}_3$ , assuming a background concentration of 40 ppb.<sup>82</sup> Together, these observations demonstrate that  $\text{O}_3$  is not responsible for any measurable loss of 4:2 FTOH in our

experiments. Consequently, the decay of 4:2 FTOH in the OFR is dominated by reaction with  $\cdot\text{OH}$  radicals. Ultimately, the atmospheric fate of FTOH is likely limited by reaction with  $\text{OH}$ ,<sup>13</sup> as more than 90% of FTOHs oxidize *via* hydrogen abstraction at the carbon adjacent to the alcohol group.<sup>80,84</sup> Both radicals are electrophilic with modest steric demands and both reactions are exothermic; thus, the abstraction behaviour of Cl atoms and  $\cdot\text{OH}$  radicals are expected to be similar.<sup>96</sup> While Cl atoms have shown to be a good surrogate for  $\cdot\text{OH}$  radicals, they are not perfect proxies due to differing regional selectivity.<sup>97</sup> This experimental setup allows the study of OH chemistry in the presence of water vapour instead of requiring Cl atoms. Consequently, the work described here contains the first measured rate constants made for the reaction between 4:2 FTOH and  $\cdot\text{OH}$  radicals at different RHs. The described OFR-PTR-ToF-MS technique is not limited by the presence of humidity, like FTIR, and can instead study chemistry under more atmospherically relevant conditions and make kinetic measurements on the timescale of seconds as opposed to minutes.<sup>98</sup> While previous research on PFCA precursors achieved good time resolution and observed similar degradation products, continuous high time resolution opens the door to study faster aspects of this gas-phase chemistry.<sup>74,75,86,99,100</sup> In an atmospheric context, humidity and light can vary on timescales of minutes to hours while the abundance of radicals can change on timescales of seconds. To observe such chemistry requires fast, *in situ* measurement techniques that capture rapidly shifting effects, which the PTR-MS is capable of.<sup>86</sup> In the context of chamber experiments, the high temporal resolution is beneficial to the observation of real-time reaction kinetics as well as the potential to detect transient intermediates. Ultimately, we suspect that while this greater time resolution may not be important for the study of all compounds, it could be beneficial for some and should be applied when possible.

## 4 Atmospheric implications/future directions

For the first time, 4:2 FTOH degradation kinetics and products were measured at varying RHs relevant to the range found in the atmosphere. The potential effects of RH on the gas-phase

Table 1 Summary of the 4:2 FTOH + OH rate constants found within this study at different RHs compared to the previously determined value under dry conditions, as well as those constants determined for the 1:2 and 6:2 FTOHs. The 4:2 FTOH  $k_{\text{obs}}$  at 22% RH is the 'original' rate constant while those at 44% and 60% RH are reported as an average of the three calculation approaches described in the main text

Analyte	Rate constant ( $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ )	RH (%)	Method	Reference
4:2 FTOH.	$(1.0 \pm 0.1) \times 10^{-12}$	22	OFR coupled to PTR-ToF-MS	This work
$\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$	$(7.4 \pm 0.8) \times 10^{-13}$	44		
	$(7.2 \pm 0.8) \times 10^{-13}$	60		
1:2 FTOH, $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$	$(1.07 \pm 0.22) \times 10^{-12}$	0	Relative rate	Ellis <i>et al.</i> , 2003
	$(8.9 \pm 0.3) \times 10^{-13}$		Pulsed laser photolysis-laser-induced fluorescence	Kelly <i>et al.</i> , 2005
	$(1.08 \pm 0.05) \times 10^{-12}$		Relative rate	
6:2 FTOH, $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OH}$	$(6.91 \pm 0.91) \times 10^{-13}$			Hurley <i>et al.</i> , 2005
	$(7.9 \pm 0.8) \times 10^{-13}$			Kelly <i>et al.</i> , 2005



kinetics of FTOHs, and PFAS in general, is not well understood within the literature and requires further investigation. Previous work has shown that RH can accelerate and decelerate the kinetics of non-fluorinated alcohols (20% to 95% RH).<sup>33–38</sup> Although the mechanism for a potential RH enhancement of 4:2 FTOH is not yet known, studies of similar molecules may provide insight into possible reaction pathways. Previous work on small alcohols (*e.g.*, ethanol and *n*-propanol) suggest that water can enhance reaction rates by forming weak complexes with both the alcohol and OH.<sup>34</sup> These complexes can increase the effective collision probability as well as stabilize the transition state, making product formation more favourable. Further evidence is needed for 4:2 FTOH, as this water-assisted effect is reaction-specific since the influence of water varies between systems,<sup>35</sup> before a plausible mechanism for the water vapour dependence in our experiments can be proposed.

The PTR-ToF-MS detected the 4:2 FTAL and the 4:2 FTCA. In the future, if calibrations can be conducted, the identified degradation products can be further investigated as a function of OH exposure or RH. Our observed rate coefficients at 22%, 44%, and 60% RH were similar in magnitude to the literature value reported at 0% RH,<sup>80</sup> although lower rates were observed at higher RH. The latter cannot be conclusively attributed to a role for water vapour in the kinetics as experimental errors inherent to the OFR and PTR-ToF-MS cannot be ruled out. The primary objective of this work was to evaluate the feasibility of combining an OFR with PTR-ToF-MS to measure PFAS oxidation kinetics and to provide initial constraints on OH reaction kinetics for 4:2 FTOH under varying RH conditions. As the RH issues experienced here do not negate the kinetic findings, the results presented in this work highlight the need for continued investigation into the role of water vapour in the atmospheric oxidation of volatile PFAS and provides a foundation for improving mechanistic understanding of these processes in future studies.

While our experimental technique allows real-time study of 4:2 FTOH oxidation under atmospherically relevant RH, several limitations should be noted. High RH can influence instrument sensitivity and may contribute to systematic biases reflected in measured rate constants. The radical chemistry within the OFR may also differ from atmospheric conditions due to elevated HO<sub>2</sub> concentrations, which can alter product distributions. Additionally, this approach is most effective for volatile or semi-volatile species with favourable PAs, making detection of stable end products such as short-chain PFCAs challenging. Complementary analytical techniques may be required to observe full degradation to terminal oxidation products. Despite these limitations, this approach provides valuable real-time constraints on early-stage PFAS oxidation chemistry by detecting intermediates and highlights directions for future improvements. Ultimately, this work demonstrates the power of the OFR-PTR-ToF-MS as a useful real-time measurement technique to study gas-phase transformations of volatile PFAS within a laboratory setting. With an ability to study atmospherically realistic oxidative chemistry at different RHs, the described instrumental setup has the potential to study

suspected, but uncharacterized, mechanisms of atmospheric PFAS formation and degradation.

## Author contributions

Alessia A. Colussi performed the chamber experiments and data analysis. Alessia A. Colussi wrote the manuscript with contributions from all authors. All authors were involved in examining and reviewing the results. All authors were involved in editing the manuscript.

## Conflicts of interest

The authors declare that they do not have any conflicts of interest associated with this work.

## Data availability

The data supporting this article has been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5em00943j>.

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