Response to the Anonymous Referee #2 Comments for the manuscript "Reaction between perfluoroaldehydes and hydroperoxy radical in the atmosphere: Reaction mechanisms, reaction kinetics modelling, and atmospheric implications**"**

Comments:

The authors have now provided their response to the comments I made based on their original submission and has modified the manuscript accordingly. They have provided three key points to describe the effect of chain elongation on reaction thermodynamics and kinetics:

1. Longer chain leads to multiple conformers (for both reactants and TSs) resulting in reduction in the multi-structure torsional anharmonicity factor and consequently decrease in rate constants by 50 % at most.
2. C_3F_7CHO shows a significantly higher pressure dependence compared to its two smaller counterparts. However, they do not provide any explanation for this anomalous behavior.
3. They develop a computational strategy based on the frozen natural orbital (FNO) approximation for the longer (or larger) compounds that provides computational efficiency.

The authors have carried out an extensive work and the work deserves publication. However, the information is incremental in nature (like, decrement in rate constant, increasing pressure dependence in one single case) and does not provide any new insight (like, change in mechanistic pathway, new atmospheric loss channels, significant change in rate constants by orders of magnitude, systematic modulation in temperature or pressure dependence with structural changes etc.) that warrants publication in atmospheric chemistry and physics. Their development of a new computational strategy to efficiently deal with bigger molecules makes this work suitable for computational chemistry related journals. Therefore, I do not recommend publication of this manuscript in atmospheric chemistry and physics based on the above comments.

Response: We agree with your views that the original article does not provide further insight into the degradation of linear perfluoroaldehydes. Therefore, in the revised article, we have done additional computations and provided a new and full analysis on the atmospheric degradation of linear perfluoroaldehydes, containing homogeneous and heterogeneous processes. We have rewritten Section 3.3 in the revised manuscript, with corresponding minor refinements incorporated into the Abstract and Conclusions to ensure consistency

Atmospheric Implications: "To provide a further insight into the atmospheric degradation pathways of linear perfluoroaldehydes, we compare the HO_2-initiated linear perfluoroaldehyde reactions with the corresponding reactions with OH and Cl atom, their photolysis and hydrolysis.

We quantitatively evaluate the relative importance of OH- versus HO_2-initiated degradation for C_2F_5CHO and C_3F_7CHO through rate ratios defined in equations (5) and (6).

$$v_1 = \frac{k_1[C_2F_5CHO][HO_2]}{k_{OH}[C_2F_5CHO][OH]} \quad (5)$$

$$v_2 = \frac{k_2[C_3F_7CHO][HO_2]}{k'_{OH}[C_3F_7CHO][OH]} \quad (6)$$

Here, k_1 and k_2 are the rate constants of HO_2 + C_2F_5CHO and HO_2 + C_3F_7CHO calculated in the present work, respectively, while k_{OH} and k'_{OH} are the corresponding rate constants of OH+ C_2F_5CHO and OH + C_3F_7CHO obtained in the literature.(Solignac et al., 2007b; Wang et al., 2007) We calculate the rate ratios using a high OH concentration of 5×10^6 molecules cm^{-3} (Lew et al., 2020) and a typical HO_2 concentration of 1.4×10^8 molecules cm^{-3} (Brasseur and Solomon, 2006). The calculated results reveal that within the temperature range of 220-320 K, the rate ratios for v_1 and v_2 are in the range of

Table 1. Rate ratios of HO_2 + C_2F_5CHO to OH + C_2F_5CHO and HO_2 + C_3F_7CHO to OH + C_3F_7CHO within the Temperature Range of 240 to 350 K.

T(K)	k_1 [a]	k'_2 [a]	v_1 [b]	v_2 [b]
220	9.04×10^{-13}	6.10×10^{-13}	79.2	45.7
240	4.64×10^{-13}	3.12×10^{-13}	34.22	20.34
260	2.68×10^{-13}	1.79×10^{-13}	17.09	10.38
280	1.70×10^{-13}	1.13×10^{-13}	9.55	5.90
298	1.19×10^{-13}	7.92×10^{-13}	6.06	3.83
320	8.21×10^{-13}	5.48×10^{-13}	3.76	2.43

[a] k_1 and k'_2 are the rate constants of the HO_2 reactions with C_2F_5CHO and C_3F_7CHO, from the literature respectively. [b] v_1 *and* v_2 denote the rate ratios of HO_2 with C_2F_5CHO and C_3F_7CHO to OH with C_2F_5CHO and C_3F_7CHO, respectively.

79.2 to 3.76 and 45.7 to 2.43, respectively. Therefore, the present findings indicate that HO_2 initiated reactions dominate over OH initiated reactions for the degradation of C_2F_5CHO and C_3F_7CHO. We further consider the atmospheric lifetimes of C_2F_5CHO and C_3F_7CHO with respect to HO_2 at 0–50 km altitude in Table 2. Rapid HO_2-initiated degradation leads to short atmospheric lifetimes of ~14.4–31.3 hours for C_2F_5CHO and 21.6–51.8 hours for C_3F_7CHO (Table 2), which are significantly shorter than the ~20-day atmospheric lifetime driven by OH oxidation at below 10 km.(Antiñolo et al., 2014)

Table 2. Hydroperoxyl radical concentration (in molecules cm^{-3}), rate constants (in cm^3 $molecule^{-1}$ s^{-1}), and atmospheric lifetimes (in hours) with respect to bimolecular reactions as functions of altitude.

H (km)[a]	T (K)[a]	P (mbar)[a]	$[HO_2]$[b]	k_1 (T, p)[c]	k_2 (T, p)[c]	τ_1[d]	τ_2[d]
0	290.2	1010	1.40×10^8	1.38×10^{-13}	9.18×10^{-14}	14.4	21.6
5	250.5	496	4.90×10^7	3.44×10^{-13}	2.30×10^{-13}	16.5	24.7
10	215.6	243	8.30×10^6	1.07×10^{-12}	6.47×10^{-13}	31.3	51.8
15	198	119	2.30×10^6	2.21×10^{-12}	2.98×10^{-13}	54.7	4.05×10^2
20	208	58.2	2.90×10^6	1.38×10^{-12}	1.22×10^{-13}	69.3	7.85×10^2
25	216.1	28.5	5.70×10^6	9.38×10^{-13}	4.32×10^{-14}	52.0	1.13×10^3
30	221.5	13.9	7.50×10^6	6.52×10^{-13}	1.29×10^{-14}	56.8	2.88×10^3

35	228.1	6.83	6.90×10^{6}	4.04×10^{-13}	4.13×10^{-15}	99.6	9.74×10^{3}
40	240.5	3.34	5.90×10^{6}	2.29×10^{-13}	1.73×10^{-15}	2.06×10^{2}	2.73×10^{4}
45	251.9	1.64	4.90×10^{6}	1.27×10^{-13}	6.56×10^{-16}	4.45×10^{2}	8.64×10^{4}
50	253.7	0.801	4.00×10^{6}	5.87×10^{-13}	1.80×10^{-16}	1.18×10^{3}	3.86×10^{5}

[a]H denotes altitude (atmospheric scale height); T denotes temperature; p denotes pressure. [b]Data are from ref (Brasseur and Solomon, 2006). [c]k_1, k_2 are the rate constants of the HO_2 reactions with C_2F_5CHO and C_3F_7CHO, respectively. [d]$\tau_1 = 1/(k_1[HO_2])$ and $\tau_2 = 1/(k_2[HO_2])$ define the atmospheric lifetimes for HO_2 reactions with C_2F_5CHO and C_3F_7CHO, respectively.

To provide further insight into the degradation of C_2F_5CHO and C_3F_7CHO under atmospheric conditions, further analysis has been done based on Geos-Chem data. GEOS-Chem simulations indicate that HO_2 concentrations reach a maximum of 4.99×10^8 molecules cm^{-3} in the Amazon region, with a mean value of 9.93×10^7 molecules cm^{-3}. (Long et al., 2024) In contrast, the maximum OH concentration over the Atlantic and Pacific oceans is found to be 8.03×10^6 molecules cm^{-3}, with an average value of 1.06×10^6 molecules cm^{-3}. (Lelieveld et al., 2016) However, the OH concentration remarkably differ from daytime to nighttime.(Bey et al., 1997; Stone et al., 2012) Therefore, we consider the concentration ratio between HO_2 and OH during the nighttime and daytime. During the nighttime, as shown in Fig. 9, the concentration ratio of $[HO_2]/[OH]$ exceeds two orders of magnitude in industrial regions such as Russia, Malaysia, and parts of Africa, with values reaching as high as 410–1,200 in the Amazon. This markedly enhances the HO_2-to-OH degradation rate ratios for C_2F_5CHO and C_3F_7CHO, reaching values of 88.5–259 and 56.0–164, respectively. This suggest that HO_2-initiated degradation exceeds OH-initiated pathways by more than a factor of 50 during nighttime in these regions. In contrast, over oceanic regions such as the Atlantic and Pacific, the $[HO_2]/[OH]$ ratio falls below unity, substantially reducing the contribution of HO_2 to degradation processes in these areas.

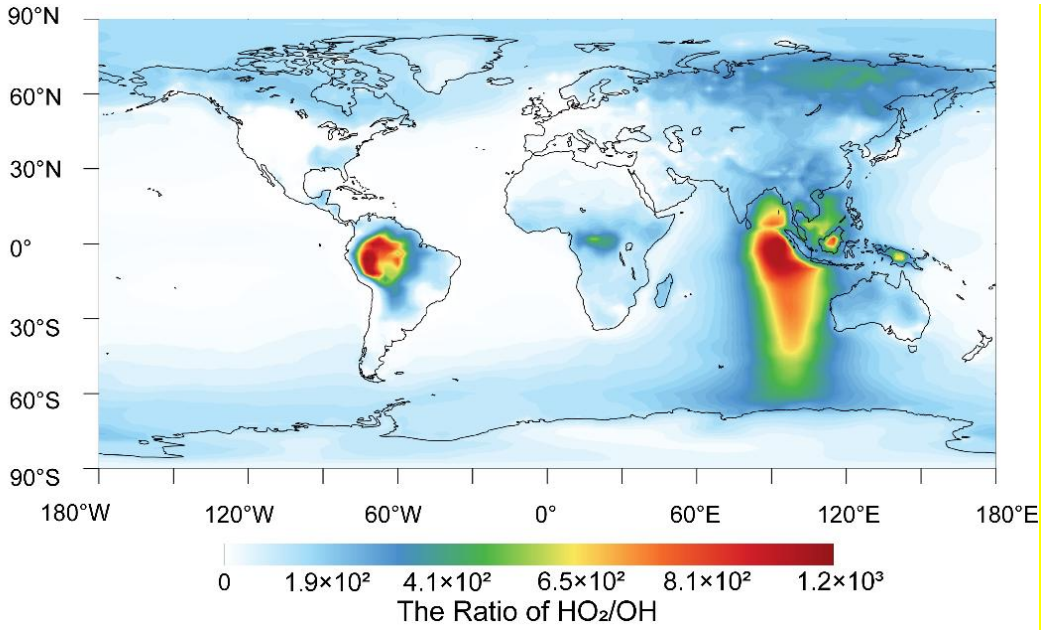

Figure 9. The annual average ratio of HO_2/OH at night globally.

During the nighttime, as shown in Figure S4, the concentration ratios between HO_2 and OH generally favor HO_2, exhibiting maxima up to three orders of magnitude along the western coast of South America and ranging from one to two orders of magnitude in industrialized and African regions. These elevated ratios are closely associated with localized emission sources. However, During the daytime, photolysis is also an important route for removal of C_2F_5CHO and C_3F_7CHO. For C_2F_5CHO and C_3F_7CHO, photolysis represents the dominant atmospheric degradation route. C_2F_5CHO exhibits a high photolysis quantum yield of 0.81 ± 0.09 at 254 nm, corresponding to an estimated atmospheric lifetime of less than two days in Table 3. Similarly, C_3F_7CHO displays a measured photolysis lifetime of 21 ± 10 hours under sunlight, confirming the efficiency of this removal mechanism.(Chiappero et al., 2006)(Solignac et al., 2007a).

Chlorine atom reactions represent an additional potential atmospheric degradation pathway for linear perfluorinated aldehydes. Kinetic measurements report rate constants of $k(Cl + C_2F_5CHO) = (1.96 \pm 0.28) \times 10^{-12}$ cm³ molecule^{-1} s^{-1} (Sulbaek Andersen et al., 2003) and $k(Cl + C_3F_7CHO) = (2.03 \pm 0.23) \times 10^{-12}$ cm³ molecule^{-1} s^{-1} (Andersen et al., 2004), which are approximately one order of magnitude higher than those for the corresponding HO_2-initiated reactions. Although Cl atoms exhibit intrinsically faster reaction kinetics, the atmospheric relevance of this degradation pathway is limited by the relatively low concentrations of Cl in the troposphere. Typical Cl atom concentrations range from 1.0×10^4 to 3.0×10^5 molecules cm^{-3} (Chang et al., 2004; Hossaini et al., 2016; Wang et al.,

2019), leading to estimated atmospheric lifetimes of approximately 400 hours (~17 days) for both C_2F_5CHO and C_3F_7CHO. This stands in sharp contrast to the significantly shorter HO_2-driven lifetimes, which are typically less than 79.2 hours in the lower troposphere in Table 3. The predominance of HO_2-mediated degradation arises from the relatively high ambient concentrations of HO_2, which compensate for its slower reaction kinetics—particularly in regions such as the Amazon, where $[HO_2]/[Cl]$ ratios may exceed ~ 10^3.(Li et al., 2018; Wang et al., 2019) Under such conditions, the HO_2 intiated reaction rate can exceed that of Cl by 2–3 orders of magnitude. Moreover, the atmospheric relevance of Cl-initiated degradation is further constrained by its spatial heterogeneity, being primarily restricted to marine boundary layers and polluted coastal environments.(Hossaini et al., 2016; Yang et al., 2022) In contrast, HO_2-driven degradation is effective across continental interiors and industrialized regions.

Table 3. Atmospheric lifetimes (τ, hours) of C_2F_5CHO and C_3F_7CHO against major degradation pathways.

Reactant/Process	C_2F_5CHO		C_3F_7CHO	
	τ (hours)	Ref.	τ (hours)	Ref.
HO_2	3.76-79.2	This work	2.43-45.7	This work
OH	90.8-174.2	(Antiñolo et al., 2014)	79.7-113.0	(Solignac et al., 2007b)
Photolysis	<48	(Chiappero et al., 2006)	14.6-39.7	(Solignac et al., 2007b)
Cl	424.4-571.6	(Sulbaek Andersen et al., 2003)	409.7-514.4	(Andersen et al., 2004)
Hydrolysis [a]	>5.39 × 10^6	This work	-	-
HCOOH catalysis [b]	>5.06 × 10^7	This work	>1.13 × 10^8	This work
Heterogeneous hydrolysis [c]	3.47× 10^{-4}	This work	-	-

[a]Gas-phase hydrolysis of C_2F_5CHO with H_2O. [b]HCOOH-catalyzed gas-phase hydrolysis of C_2F_5CHO/C_3F_7CHO with H_2O. [c]Hydrolysis of C_2F_5CHO with water dimer at the air-water interface.

In addition to photolysis and radical-initiated oxidation, hydrolysis constitutes another potential atmospheric sink for C_2F_5CHO and C_3F_7CHO. Taking C_2F_5CHO hydrolysis as an example, its gas phase hydrolysis proceeds extremely slowly, with an estimated atmospheric lifetime exceeding 5.39 × 10^6 hours (Table 3 and Table S11). This removal pathway is negligible, aligning with findings reported for CF_3CHO.(Sulbaek Andersen et al., 2006) Hydrolysis catalyzed by atmospheric acids could potentially enhance hydrolysis rates through its ability to reduce the reaction barriers.(Hazra et al., 2013; Liu et al.,

2021) Formic acid (HCOOH), a ubiquitous atmospheric component, forms stable complexes with water ($HCOOH\cdots H_2O$). Even at elevated concentrations of $HCOOH\cdots H_2O$ complexes (e.g., 10^{11} molecule cm^{-3}), the estimated hydrolysis lifetimes of C_2F_5CHO and C_3F_7CHO exceed 10^7 hours in Table 3. These timescales remain orders of magnitude longer than those associated with HO_2-initiated degradation, suggesting that the acid-catalyzed hydrolysis is insufficient to promote significant atmospheric removal of these compounds. Therefore, although acid catalysis effectively reduces the reaction barrier, its impact on the gas-phase degradation of C_2F_5CHO and C_3F_7CHO is negligible under typical tropospheric conditions.

Hydrolysis at air–water interfaces, such as those present on aerosol particles and cloud droplets, proceeds with markedly enhanced efficiency. Laboratory experiments have shown that passing gaseous CF_3CHO through liquid water results in over 80% conversion to $CF_3CH(OH)_2$ within seconds, highlighting the potential importance of heterogeneous processes in atmospheric removal pathways.(Sulbaek Andersen et al., 2006) Similarly, ^1H NMR measurements reveal that C_2F_5CHO rapidly converts to its gem-diol form, $CF_3CF_2CH(OH)_2$, within 3 minutes upon contact with liquid water, further confirming the efficient aqueous-phase hydration of perfluorinated aldehydes. (Sulbaek Andersen et al., 2006) Here, we estimate a low Gibbs free-energy barrier (ΔG = 9.8 kcal/mol) for $C_2F_5CHO + 3H_2O$ at air-water interfaces, proceeding via a cyclic proton-transfer mechanism by using ab initio molecular dynamics, compared to a much higher barrier of 25.5 kcal/mol for the corresponding gas-phase reaction (See Figure S5a, b). More details are provided in Supplementary Material. This results in significantly shorter atmospheric lifetimes, on the order of 3.47×10^{-4} hours. Under humid conditions, such air–water interfacial hydrolysis is likely to dominate and may effectively compete with HO_2-mediated degradation pathways. Once formed, $C_nF_{2n+1}CH(OH)_2$ reacts with OH, ultimately leading to the formation of perfluorocarboxylic acids (PFCAs). This hydrolysis-oxidation pathway represents a significant indirect source of persistent PFCAs, particularly given the ubiquity of aqueous phases in the atmosphere.

We can conclude that HO_2 intiated degradation pathways dominate the gas-phase degradation of C_2F_5CHO and C_3F_7CHO. We further consider the final prodcut in the $HO_2 + C_nF_{2n}CHO$ reactions. As mentioned, the HO_2 reaction generates intermediate perfluoroalkyl radicals C_nF_{2n+1}, which can subsequently undergo a carbon-shortening process to form the more stable COF_2, as depicted in Figure 10. Taking the example of C_2F_5, the process starts with C_2F_5 reacting with O_2 to form $C_2F_5O_2$. Subsequently, $C_2F_5O_2$ reacts with NO to produce C_2F_5O, which then undergoes C-C bond cleavage to

generate CF_3 and COF_2. The CF_3 further reacts to eventually yield COF_2 through a similar reaction pathway. However, the absence of quantified rate constants for these reactions prevents a robust assessment of their global or regional impacts. A comprehensive evaluation of the role of NO would require integrating the kinetics of RO_2 + NO reactions (e.g., M1/M2 + NO) into atmospheric models, which is beyond the scope of this study.

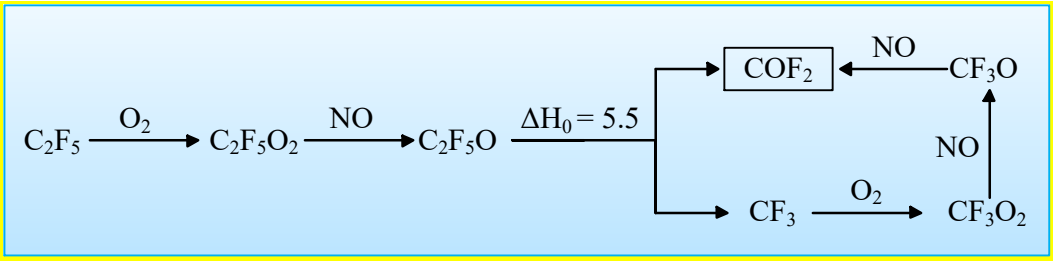

Figure 10. Atmospheric degradation mechanism for C_nF_{2n+1} with C_2F_5 used as a representative example.

In summary, we identify that the HO_2-initiated reaction represents an important atmospheric sink for linear perfluoroaldehydes in gas phase. Notably, recent studies suggest that HO_2 concentrations may be elevated at air–water interfaces compared to the bulk gas phase.(Angelaki et al., 2024; Li et al., 2023) Given the enhanced reactivity at the air–water interface and the complex competition between OH and HO_2, interfacial HO_2-driven degradation may play a more significant role than previously recognized, potentially influencing atmospheric acidity. For example, Xia et al. (2024) recently reported both single-carbon and double-carbon scission pathways during the degradation of C_7F_{15} on water droplet surfaces. These heterogeneous processes may contribute not only to the atmospheric removal of perfluoroaldehydes but also to the broader degradation of polyfluoroalkyl substances (PFAS). Nevertheless, further experimental and theoretical studies on reaction kinetics and mechanisms are needed to better constrain this complex chemical processes. Incorporating such processes into atmospheric models is crucial for improving the prediction of PFAS environmental fate and secondary pollution, with important implications for emission control strategies and environmental risk assessment. ”

(page 12-17, lines 270-383)

Abstract: “…pressures ranging from 0.026 to 2.3 bar across a temperature range of 190–350 K. Furthermore, atmospheric lifetimes of C_2F_5CHO and C_3F_7CHO are discussed based on the homogenous and heterogeneous processes. Our findings also reveal that the reactions of C_2F_5CHO and C_3F_7CHO with HO_2 radicals dominate over those with OH radicals in Russia, Malaysia, parts of Africa by the calculated

results in combination with data based on global atmospheric chemical model simulations. HO_2-initiated degradation represents a major atmospheric sink, compared to photolysis and Cl-initiated oxidation in gas phase at night, whereas hydrolysis at air-water interface plays a critical role in the sink of linear perfluoroaldehydes." (page 1, lines 16-17, and 19-21)

Summarizing Remarks: "…shorter than that of the corresponding OH-mediated pathways. In addition, photolysis, typically occurring within 48 hours, represents an efficient daytime removal pathway, while heterogeneous hydrolysis proceeds rapidly at the air-water interfaces with characteristic timescales of less than 1 hour. Accordingly, HO_2-initiated degradation should be considered a major gas-phase sink, particularly in continental source regions." (page 17, lines 398-401)

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