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"

We sincerely appreciate the time and effort dedicated to reviewing our manuscript. We thank the reviewers for their constructive feedback, which has helped us improve the clarity and impact of our work. Below, we address your concerns and provide a point-by-point response to your comments. Reviewer comments (RC) are in black font and author comments (AC) are in blue.

Zegang Dong and coworkers have carried out an extensive theoretical investigation on the gas phase reaction between two perfluoroaldehydes and hydroperoxyl radical and estimated their atmospheric implications. The work is extensive, the theoretical model is well chosen and already shown to be appropriate for similar class of reactions, the results are properly presented and explained.

Response: Thank you for your positive comments.

However, the work falls severely short in originality and fails to provide any new insight, and is simply an extension of their earlier work (*J. Am. Chem. Soc.* 2022, 144, 19910−19920). Both the reactions studied here are close replica, mechanistically, energetically and kinetically, of the reaction between CF_3CHO and HO_2 studied in their previous work. As the reactions are always centered at the carbonyl group of reacting aldehydes, with no involvement of the side chains, this is very much expected that a mere elongation of the side chain would not have any dramatic effect on the reactions.

Response: Thank you for your comments. We agree with your view that the present work is based on our previous investigations. We do not agree with your view that the elongation of the side chain would not have any dramatic effects on the reactions. In fact, there are two important influences on reaction thermodynamics and kinetics.

First, longer chain for perfluoroaldehydes leads to producing multiple conformers in both reactants and transition states (See Figures 3, S1, and S3), with different energy distributions for these conformers, spanning 0-1.7 and 0-1.9 kcal/mol, respectively. This leads to a reduction in the multi-structure torsional anharmonicity factor ($F_2^{\text{MS-T}}$) to 0.45–0.52, compared to 1.0 in one conformer systems in our previous article, resulting in a 50% decrease in rate constants relative to single-conformer C_3F_7CHO and a 34–43% decrease relative to CF_3CHO. This effect has not been observed in our previous study (*J. Am. Chem. Soc.* **2022**, *144*, 19910–19920), which cannot be obtained without further investigations. Additionally, for larger molecules such as C_4F_9CHO and $C_5F_{11}CHO$, the increased molecular size and number of conformers (e.g., 36 conformers in the transition state of $C_5F_{11}CHO$ with energy distributions up to 4.8 kcal/mol) further complicate the potential energy surface calculations. These findings highlight that the conformational diversity and molecular size effects significantly alter reaction kinetics, even when the enthalpy of activation remains relatively insensitive to chain length.

Second, C_3F_7CHO + HO_2 exhibits remarkably pressure dependence, with transition pressures ($p_{1/2}$) ranging from 0.026 to 2.3 bar at 190 – 350 K (See Figure 8, Table S10). This contrasts sharply with CF_3CHO + HO_2, where pressure dependence is negligible. These findings demonstrate that extending the side chain not only have important influences on reaction kinetics through conformational diversity, but also causes pressure-dependent behavior that cannot be captured by simple empirical models. These findings deepen our understanding of the atmospheric chemistry of polyfluoroalkyl substances (PFAS) and provide critical theoretical foundations for modeling the degradation kinetics of complex PFAS compounds.

Third, this study addresses the challenges on high-accurate quantum chemical calculations for longer linear polyfluorinated aldehydes by developing a computational strategy based on the frozen natural orbital (FNO) approximation, specifically the FNO-CCSD(T)-F12/cc-pVDZ-F12 method. In the present work, we also find that this approach significantly provides computational efficiency and reaches sub-kcal/mol (<1 kcal/mol) accuracy, enabling to predict the enthalpies of activation at 0 K from short-chain to long-chain molecules. Therefore, we believe that the present work has provided new insights on how to obtain the quantitative kinetics of perfluoroaldehydes and hydroperoxy radical.

In our initial manuscript, some key issues may not be clarified; this leads to unclearly revealing the originality and new insights into the present work. Therefore, in the revised article, we have done many corrections to improve the manuscript.

(1) We have rewritten the abstract, “Linear perfluoroaldehydes are important products formed in the atmospheric oxidation of industrial fluorinated compounds. However, their atmospheric lifetimes are incompletely known. Here, we employ high level quantum chemistry methods and a dual-level strategy for kinetics to probe the reactions of C_2F_5CHO and C_3F_7CHO with HO_2. Our calculated results unveil almost equal activation enthalpies at 0 K for perfluoroaldehyde reaction with HO_2, indicating that the carbon chain length minimally influences reaction thermodynamics. Interestingly, the present findings reveal that anharmonicity remarkably enhances the reaction rate constant, whereas multi-structural anharmonicity, recrossing, and tunnelling effects exhibit lesser impacts in the C_2F_5CHO/C_3F_7CHO + HO_2 reaction. In particular, the atmospheric lifetimes for C_2F_5CHO and C_3F_7CHO, approximately 14.4-31.3 hours and 21.6-51.8 hours by HO_2 are much shorter than those via OH radical, underscoring the dominant removal role of HO_2 toward C_2F_5CHO and C_3F_7CHO in the atmosphere. Since GEOS-Chem simulation shows that the concentration of HO_2 is at least 10^2 times higher than that of OH radical in Russia, Malaysia, and parts of Africa, the reactions of C_2F_5CHO and C_3F_7CHO with HO_2 radicals dominate over those with OH radicals and play more vital role in the atmospheric chemical processes of these regions. This study enhances our understanding of the chemical transformations of linear perfluoroaldehydes and provides a scientific foundation for strategies aimed at mitigating their emissions.” has been corrected into “Linear perfluoroaldehydes are important products formed in the atmospheric oxidation of industrial fluorinated compounds. However, their atmospheric lifetimes are incompletely known. Here, we employ high level quantum chemistry methods and a dual-level strategy for kinetics to investigate the reactions of C_2F_5CHO and C_3F_7CHO with HO_2. Our calculated results unveil almost equal activation enthalpies at 0 K for linear perfluoroaldehyde reaction with

HO_2, indicating that the carbon chain length negligibly influences reaction thermodynamics. The calculated kinetics reveal that vibrational anharmonicity enhance rate constants by a factor of 3–10, while torsional anharmonicity reduces rate constants by 34–55%. Additionally, we also find that the reaction of C_3F_7CHO with HO_2 exhibits significant pressure dependence, with transition pressures ranging from 0.026 to 2.3 bar across a temperature range of 190–350 K. Furthermore, 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. These findings establish chain-length-dependent pressure effects and conformational sampling as critical, previously unrecognized factors in kinetics calculations, providing a framework for modelling complex fluorotelomer transformations and guiding emission mitigation strategies." on page 1.

(2) In section 1 (Introduction), we have revised the sentence from "Nevertheless, the importance of sink pathway by HO_2 is still unknown because there have not been kinetics data for linear perfluoroaldehydes with HO_2 in the literature." to "Nevertheless, the importance of sink pathway by HO_2 is still unknown because there have not been kinetics data for linear perfluoroaldehydes with HO_2 in the literature. Moreover, chain elongation may have influences on reaction kinetics due to multiple conformers. Furthermore, it is unknown for the pressure-dependent effects of larger perfluoroaldehydes with HO_2. Although our previous investigations have revealed the importance of CF_3CHO + HO_2 in the atmosphere (Long et al., 2022), their kinetics of larger perfluoroaldehydes with HO_2 are further required to investigate due to the unique features that depend on the specific reaction systems such as multi-structural anharmonicity and pressure effects in these complex systems. Additionally, it is a big challenge for addressing the larger perfluoroaldehydes with HO_2 because the computational cost grows very rapidly with system size, making such calculations impractical for high-level quantum chemistry methods." on page 2-3

We also revised the sentence from "These findings could hold significant implications for the formation and yield of HCOOH, thereby contributing to the broader discourse on atmospheric chemistry and environmental policy." to "This study not only resolves the knowledge gap regarding HO_2-initiated oxidation of linear perfluoroaldehydes but also establishes a computational strategy for predicting the atmospheric fates of long-chain PFAS derivatives. Our findings provide critical insights for refining emission control strategies and mitigating the environmental persistence of these compounds." on Page 3

(3) In section 2.1 (Options for electronic structure density functionals), we have added some sentences "… were used to calculate single-point energies. The FNO-CCSD(T) approach that significantly improves computational efficiency with cost reduction of up to an order of magnitude was utilized to calculate larger systems." on Page 3

(4) In section 3.1 (Results and discussion), We have added some sentences for discussion

"…, aiming to investigate the effects of increasing carbon chain length on the enthalpy of activation at 0 K. The calculated results show a deviation of only 0.2 kcal/mol in activation enthalpy at 0 K between FNO-CCSD(T)-F12//cc-pVDZ-F12 (-2.6 kcal/mol) and CCSD(T)-F12a/cc-pVTZ-F12 (-2.4 kcal/mol) in $CF_3CHO + HO_2$, validating the robustness of FNO-CCSD(T)-F12//cc-pVDZ-F12 for complex fluorinated systems." on Page 7

"For instance, C_2F_5CHO exhibits three transition state conformers with energy differences spanning 0–1.7 kcal/mol, while C_3F_7CHO has five conformers distributed over 0–1.8 kcal/mol. This trend amplifies for longer chains: $C_5F_{11}CHO$ generates 36 distinct conformers in its transition state, with energy variations extending up to 4.8 kcal/mol." on Page 8

We also added an additional paragraph: "Our further analysis of the global distribution of the ratio between HO_2 and OH during daytime reveals that HO_2 concentrations are generally higher than those of OH (see Figure S4). Notably, along the west coast of South America (approximately between 0° and 30°S latitude and 60°W to 120°W longitude), the ratio can reach up to three orders of magnitude. Industrial areas (such as Russia and Malaysia) and certain regions in Africa also exhibit high ratios of 1-2 orders of magnitude. This suggests that in these areas, the concentration of HO_2 is significantly higher than that of OH, which may be related to local industrial activities or specific emission characteristics. However, due to the presence of daytime photolysis, the generation and loss pathways of HO_2 and OH become more complex, leading to significant uncertainty in interpreting the ratio. For instance, photolysis can alter the formation rates of HO_2 and OH, thereby affecting their concentration ratio. Additionally, the high ratios along the eastern coast of North America may be associated with atmospheric transport and regional emission features. Despite these complexities, the high daytime ratios still indicate that in specific regions, HO_2 may play a role in the oxidation pathways of C_2F_5CHO and C_3H_7CHO both during the day and at night. Future research should integrate observational data with model refinements to better quantify the impact of photolysis on the HO_2/OH ratio." on Page 14

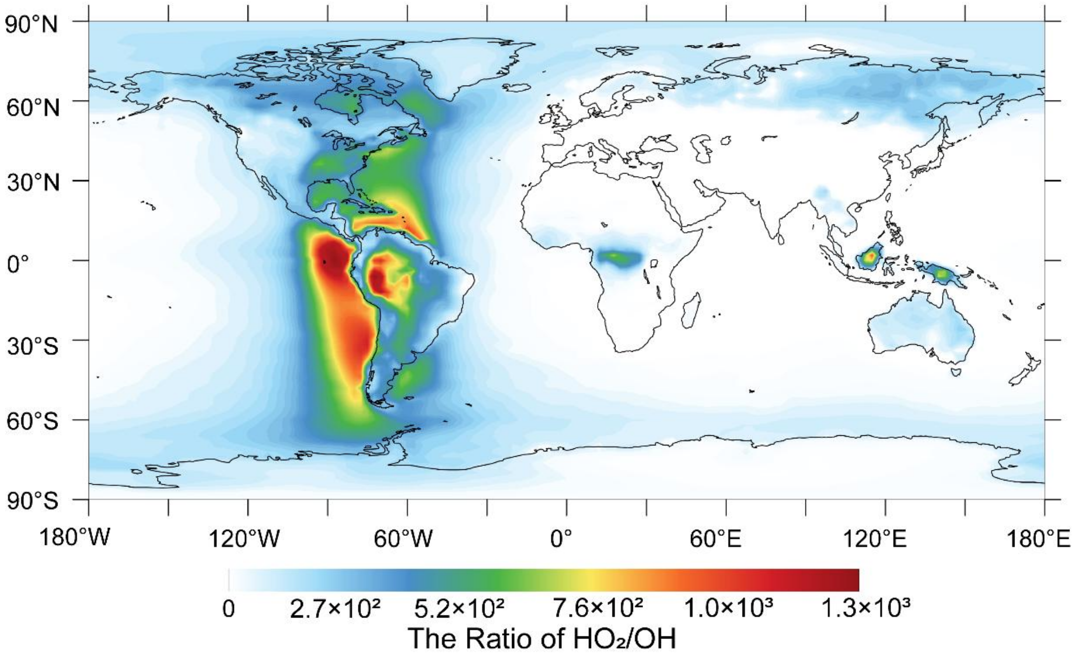

Figure S4. The annual average ratio of HO_2/OH during the day globally. (In Supplement)

(5) In section 4 (Summarizing Remarks), we have revised some sentences from "We construct a comprehensive reaction potential energy surface and find that the activation enthalpies for the reactions of C_2F_5CHO and C_3F_7CHO with HO_2 at 0 K are both -2.7 kcal/mol, which are exactly the same. Our calculated results suggest that the elongation of the carbon chain in linear perfluorinated aldehyde molecules has a negligible effect on the activation enthalpy." to "We find that the activation enthalpies for the reactions of C_2F_5CHO and C_3F_7CHO with HO_2 at 0 K are both -2.7 kcal/mol, demonstrating that carbon chain elongation in linear perfluoroaldehydes has a negligible thermodynamic influence on their enthalpies of activation at 0 K. This is further shown in C_4F_9CHO and $C_5F_{11}CHO$ with HO_2." on page 15

Revised the sentences from "Additionally, we compared these reactions with the primary oxidation pathway of linear perfluoroaldehydes—their reaction with hydroxyl radicals. We find that there is a big ratio between HO_2 and OH concentrations in the Amazon region. The comparative results suggest that the reactions of HO_2 with C_2F_5CHO and C_3F_7CHO may dominate their atmospheric chemistry in the Amazon region, thereby affecting the environmental impact of these compounds. Based on our estimates, the atmospheric lifetimes of C_2F_5CHO and C_3F_7CHO are 14.4-31.3 hours and 21.6-51.8 hours, respectively, and under NO conditions this pathway may be a source of HCOOH and COF_2 in the troposphere." to "By integrating kinetics with the data based on GEOS-Chem modelling, we have identified some regions such as Russia, Malaysia, and parts of Africa, where HO_2 concentration exceeds OH concentration by 2–3 orders of magnitude. Therefore, the reactions of HO_2 with C_2F_5CHO and C_3F_7CHO can compete well with their corresponding reaction with OH. Specifically, the atmospheric lifetimes of C_2F_5CHO and C_3F_7CHO via HO_2 are shortened to be 14.4–31.3 h and 21.6–51.8 h, respectively, with orders of magnitude shorter than that of the corresponding OH-mediated pathways (>20 days). Under high NO_x conditions, this pathway may contribute to tropospheric HCOOH and COF_2 formation." on page 15-16

The only new analysis that is available in this work is a GEOS-Chem based atmospheric modelling of the studied reactions to estimate their atmospheric implications. However, that analysis also does not provide any new information that was not known from the work cited above. Similar to CF_3CHO, the two larger perfluoroaldehydes studied here also show that reaction with HO_2 is more dominant atmospheric removal process compared to reaction with OH.

Therefore, the conclusion that this work "provide new insight into atmospheric degradation of linear perfluorinated aldehydes by HO_2 radical" is not supported by the results at all. At most, the study provides new data that shows the atmospheric degradations of larger perfluoroaldehydes by HO_2 are very similar to that of CF_3CHO which has already been reported earlier.

Response: We thank the reviewer for their feedback and agree that the dominance of HO_2 as a degradation pathway for linear perfluoroaldehydes aligns with prior observations on smaller analogs like CF_3CHO. However, by calculating the HO_2-to-OH degradation rate ratios below.

$$v_1 = \frac{k_1[\mathrm{HO_2}]}{k_{\mathrm{OH}}[\mathrm{OH}]}, v_2 = \frac{k_2[\mathrm{HO_2}]}{k'_{\mathrm{OH}}[\mathrm{OH}]}$$

According to the equation above, the rate ratios are largely determined by the ratio of the concentrations of HO_2 and OH. However, their concentrations are varied from one region another region. Geos-Chem analysis can provide further insight into their concentration distribution. For example, in the Amazon, Malaysia, and part of the Africa, elevated $[HO_2]/[OH]$ ratios are 410–1,200, which lead to the rate ratios of 88.5–259 for v_1 and 56.0–164 for v_2. In contrast, over oceanic regions like the Atlantic and Pacific, these ratios can drop below 1.

These results are remarkably different from the assumption that the concentrations of HO_2 and OH are not dependent on the specific region. Such spatial distribution, driven by localized oxidant, provides novel insights into the atmospheric processing of long-chain PFAS compounds in tropical environments. Thus, while the general dominance of HO_2 is acknowledged, our work uniquely quantifies its regional significance, offering new perspectives on the atmospheric degradation of perfluorinated aldehydes.

In order to better present our research results, in the revised manuscript, we modified the sentence from "Especially in the parts of Africa, HO_2 is even three orders of magnitude higher than OH. In addition, high concentration ratios have been observed along the Indian Ocean margin near Indonesia, which may be due to atmospheric transport. This large concentration ratios between HO_2 and OH suggests that HO_2 leads to sink of C_2F_5CHO and C_3H_7CHO at night in these particular regions." to "Specifically, in parts of Africa, HO_2 concentrations are even three orders of magnitude higher than that of OH. Additionally, high HO_2/OH ratios have been observed along the Indian Ocean margin near Indonesia, which may be attributed to atmospheric transport and enhanced HO_2 production from industrial activities. In the Amazon region, the $[HO_2]/[OH]$ ratio can reach as high as 410–

1,200. This significantly increases the HO_2-to-OH degradation rate ratios for C_2F_5CHO and C_3F_7CHO, reaching 88.5–259 and 56.0–164, respectively. These rate ratios indicate that HO_2-driven degradation exceeds OH-mediated degradation by over 50 times. This large concentration ratios between HO_2 and OH suggests that HO_2 leads to sink of C_2F_5CHO and C_3H_7CHO at night in these regions. In contrast, over oceanic regions like the Atlantic and Pacific, the $[HO_2]/[OH]$ ratios drop below 1, leading to a diminished role of HO_2 in these areas." on page 13

The most baffling aspect of this work is the sudden introduction of NO into the reaction scheme and an attempt to show the title reaction as a source of formic acid and COF_2. However, there is no attempt to calculate the rate constant of the reactions involving NO, which would be required to have any realistic estimate of the importance of NO in determining the atmospheric fate of the studied perfluoroaldehydes. Therefore, the conclusion that "under NO conditions this pathway may be a source of HCOOH and COF_2 in the troposphere" is completely unfounded without proper kinetic analysis, including lifetime calculations, of these reaction channels.

Response: We appreciate the reviewer's feedback on this point. The inclusion of NO aligns with its established atmospheric relevance as a mediator in radical-driven oxidation cycles, where RO_2 + NO reactions are key sinks for peroxy radicals, forming nitrates or terminating chains.(Berndt et al., 2015; King et al., 2001; Nie et al., 2023; Orlando et al., 2000; Vereecken and Peeters, 2009) Our work extends this pattern to perfluoroalkyl systems, demonstrating analogous pathways for M1/M2 ($C_2F_5CH(O)OO/C_3F_7CH(O)OO$) reacting with NO ($\Delta H_0$ = −9.9/−11.5 kcal/mol at 0 K), reflecting thermodynamic trends in hydrocarbon systems. While detailed kinetics (e.g., rate constants) are essential for quantifying atmospheric impacts, our research focus on identifying thermochemically pathways (e.g., Vereecken & Peeters, 2009, using SAR models to prioritize key channels). The subsequent decomposition of intermediates $C_2F_5CH(O)OH/C_3F_7CH(O)OH$ exhibits low barriers (4.7–5.6 kcal/mol at 0 K), suggesting rapid dissociation under tropospheric conditions. However, as emphasized in Section 3.3, the lack of experimental rate constants for perfluoroalkyl-oxy systems precludes definitive quantification of HCOOH/COF_2 yields, highlighting the need for future kinetic validation. We have revised the manuscript to clarify the reviewer's concern. Specifically, we have modified the following sections:

3.1. The electronic structure of the $C_2F_5CHO/C_3F_7CHO + HO_2$ reaction: "As depicted in Figure S2, M1 and M2 undergo initial reactions with NO to yield the products $C_2F_5CH(O)OH$, $C_3F_7CH(O)OH$, and NO_2, exhibiting activation enthalpies of –9.9 and –11.5 kcal/mol at 0 K, respectively. These results are consistent with previous studies on similar reactions involving RO_2 + NO. (Berndt et al., 2015; King et al., 2001; Nie et al., 2023; Orlando et al., 2000; Vereecken and Peeters, 2009) These products then undergo unimolecular reactions to decompose into C_2F_5 and C_3F_7 radicals and formic acid in Figure 2. Notably, the unimolecular decomposition of $C_2F_5CH(O)OH$ and $C_3F_7CH(O)OH$ represents the rate-determining step of the overall reaction, with corresponding activation enthalpies of 5.6 kcal/mol and 4.7 kcal/mol (0 K), respectively; this indicates that formic acid may potentially be formed via C_2F_5CHO/C_3F_7CHO + HO_2 in the presence of high concentration NO in the atmosphere." on page 6-7

3.3 Atmospheric Implications: "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." on page 14-15

4. Summarizing Remarks: "Therefore, the reactions of HO_2 with C_2F_5CHO and C_3F_7CHO can compete well with their corresponding reaction with OH. Specifically, the atmospheric lifetimes of C_2F_5CHO and C_3F_7CHO via HO_2 are shortened to be 14.4–31.3 h and 21.6–51.8 h, respectively, with orders of magnitude shorter than that of the corresponding OH-mediated pathways (>20 days). Under NO-rich conditions, the reaction pathway involving HO_2-initiated oxidation of perfluoroaldehydes may serve as a potential source of HCOOH and COF_2 in the troposphere." on page 15-16

References Added in Revision:

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Vereecken, L. and Peeters, J.: Decomposition of substituted alkoxy radicals - Part I: A generalized structure-activity relationship for reaction barrier heights, Physical Chemistry Chemical Physics, 11, 9062–9074, https://doi.org/10.1039/b909712k, 2009.