

Reaction between linear perfluoroaldehydes and hydroperoxy radical in the atmosphere: Reaction mechanisms, reaction kinetics modelling, and atmospheric implications

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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 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.

1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are highly fluorinated compounds with long atmospheric lifetimes, which have important influences on global warming potential (GWP) and environmental health.(Ackerman Grunfeld et al., 2024; Rupp et al., 2023; Sznajder-Katarzyńska et al., 2019; Wu et al., 2024) During their degradation in the atmosphere, PFASs undergo complex chemical transformations, leading to the formation of linear perfluoroaldehydes. (Alam et al.,2024; Burkholder et al., 2015; David et al., 2021; Wang et al., 2021, 2024) Linear perfluoroaldehydes ($C_nF_{2n+1}CHO$) are significant intermediate compounds, which belong to the aldehydes family of PFASs.(Li et al., 2024; Thackray et al., 2020) Chlorofluorocarbons (CFCs) and their temporary replacements, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons

30 (HFCs), and hydrofluoroolefins (HFOs) are the important source of the linear perfluoroaldehydes.(Burkholder et al., 2015; Hurley et al., 2006; Martin et al., 2005; Rand and Mabury, 2017; Wang et al., 2023; Waterland and Dobbs, 2007) For example, under low NO_x conditions, the reaction of OH radicals with the potential foaming agent CF₃(CF₂)₂CH=CH₂ (HFC-1447fz) leads to the formation of C₃F₇CHO.(Jiménez et al., 2016; Yu et al., 2024) Furthermore, the atmospheric chemical processes of linear perfluoroaldehydes are of key importance for determining the atmospheric oxidation of fluorotelomer alcohols
35 (FTOHs).(Antiñolo et al., 2012; Hurley et al., 2004)

Linear perfluoroaldehydes were generally considered to be removed through photochemical reactions (Chiappero et al., 2006; Kelly et al., 2004) and free radical reactions initiated by OH and Cl radicals (Andersen et al., 2004; Chiappero et al., 2010; Wang et al., 2007). Additionally, NO₃ may also contribute to their atmospheric degradation. (Burkholder et al., 2015; Ziemann and Atkinson, 2012) During the daytime, photolysis of linear perfluoroaldehydes was considered to be the dominant
40 removal process for C_nF_{2n+1}CHO, with estimated atmospheric lifetimes ranging from hours to several days.(Antiñolo et al., 2014; Chiappero et al., 2006) Antiñolo et al. (2014) reported that the photolysis lifetime of C₂F₅CHO is expected to be 3.5 hours at 273 K, with the main degradation products of CF₃CFO and COF₂. In addition, previous investigations have shown that the length of the carbon chain in C_nF_{2n+1}CHO significantly affects the quantum yield of photolysis.(Chiappero et al., 2006; Kelly et al., 2004) During the nighttime, the reactions of free radicals with C_nF_{2n+1}CHO were considered to be the major
45 degradation pathways. However, previous studies reported relatively slow rate constants for the reaction between OH and C_nF_{2n+1}CHO (n=1-4) with the values of $(6.5 \pm 1.2) \times 10^{-13}$, $(5.57 \pm 0.07) \times 10^{-13}$, $(5.8 \pm 0.6) \times 10^{-13}$, and $(6.1 \pm 0.5) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, respectively, at 298 K.(Andersen et al., 2004; Antiñolo et al., 2014; Solignac et al., 2007) This corresponds to a longer atmospheric lifetime > 20 days for these linear perfluoroaldehydes. Moreover, the rate constant of Cl atoms with C_nF_{2n+1}CHO (n = 1–4) is approximately 2×10^{-12} cm³ molecule⁻¹ s⁻¹. This value is slightly faster than that of the corresponding
50 OH radical reactions under similar conditions.(Andersen et al., 2004; Sulbaek Andersen et al., 2003) The long atmospheric lifetimes of C_nF_{2n+1}CHO provide an opportunity for other atmospheric oxidation processes of C_nF_{2n+1}CHO by other atmospheric oxidants.

HO₂ radicals are of ubiquitous active species in the atmosphere with the concentration being two orders of magnitude higher than that of OH radicals.(Bottorff et al., 2023; Gao et al., 2024a; Sascha et al., 2019; Zhang et al., 2019, 2024a, 2022)
55 Moreover, previous investigations have shown that the reactions of aldehydes with HO₂ affect the degradation process of aldehydes.(Hermans et al., 2005; Sascha et al., 2019; Zhou et al., 2024a) Additionally, global three-dimensional chemistry-transport model calculations suggest that the oxidation reactions of formaldehyde and acetone initiated by hydroperoxyl radical contribute to 30% loss of formaldehyde and acetone at the tropical troposphere.(Hermans et al., 2005) Nevertheless, the importance of sink pathway by HO₂ is still unknown because there have not been kinetics data for linear perfluoroaldehydes
60 with HO₂ 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 HO₂. Although our previous investigations have revealed the importance of CF₃CHO + HO₂ in the atmosphere (Long et al., 2022), their kinetics of larger perfluoroaldehydes with HO₂ 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 HO₂ because the computational cost grows very rapidly with system size, making such calculations impractical for high-level quantum chemistry methods.

In this article, we have investigated the reactions of HO₂ with linear perfluoroaldehydes C_nF_{2n+1}CHO (n = 2-5), specifically focusing on C₂F₅CHO and C₃F₇CHO, referred to as reactions (R1) and (R2) respectively. To delve into these reactions, high-level quantum chemistry calculation close to CCSDT(Q) accuracy in conjunction with dual-level strategy were performed to obtain their quantitative kinetics. Simultaneously, to provide further insight into kinetics, we detailly evaluated the impact of various parameters, including torsional anharmonicity, anharmonicity on the reaction kinetics over atmosphere-related temperatures and pressures. In addition, the chemical transformation of the formed intermediate products has been discussed in reactions R1 and R2. We further estimate the enthalpies of activation at 0 K for the larger-sized reactions of longer-chain perfluoroaldehyde with HO₂. Moreover, we also discuss the importance of these reactions R1 and R2 by combining the calculated reaction kinetics with global atmospheric modelling. The current results not only provide a comparative analysis with the kinetics of analogous OH-initiated reactions and photolytic processes, but also extend our understanding of the role of HO₂ in modulating the atmospheric lifetime of linear perfluoroaldehydes. This study not only resolves the knowledge gap regarding HO₂-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.



2. Computational methods and atmospheric modelling

2.1 Options for electronic structure density functionals

Our goal is to establish a precise set of electronic structure and kinetic calculation methods for the XCHO + HO₂ reaction, delivering satisfactory quantitative results. (Long et al., 2022) This previous study indicated that the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S theoretical methods can make good agreement with beyond-CCSD(T) results for the similar reaction of HCHO + HO₂. (Long et al., 2022) Furthermore, CCSD(T)-F12a/cc-pVTZ-F12 has been shown good performance for molecules containing fluorine atoms. (Dong et al., 2021; Long et al., 2022; Xia et al., 2024) Consequently, we intend to utilize the well-validated methods in the present investigations in reactions R1 and R2. Specifically, the M06-2X (Zhao and Truhlar, 2008b, a) density functional with the MG3S (Lynch et al., 2003) basis set was employed to optimize the geometries, while CCSD(T)-F12a (Adler et al., 2007; Knizia et al., 2009)/cc-pVTZ-F12 for R1 and R2 and FNO-CCSD(T)-F12 (Gyevi-Nagy et al., 2021; Taube and Bartlett, 2008)/cc-pVDZ-F12 for other C_nF_{2n+1}CHO + HO₂ (n = 1 - 5) 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

95 magnitude was utilized to calculate larger systems. Furthermore, intrinsic reaction coordinate (IRC) calculation was done to determine the correct transition states by examining the connections of each saddle point to its corresponding minima.(Hratchian and Schlegel, 2004, 2005; Kenyon, 1968)

2.2 Vibrational frequencies

We found that standard scale factor is actually not applicable for some transition states in previous investigation, so we
100 used two scale factors.(Zheng et al., 2014, 2015) The standard scale factor for M06-2X/MG3S is 0.970. Furthermore, we also calculated the specific reaction scale factors to assess the effects of anharmonicity. The reaction-specific scale factors were obtained by using the MPW1K/6-311+G(2df, 2p) electronic structure method based on the hybrid degeneracy-corrected second-order vibrational perturbation theory (HDCVPT).(Bloino et al., 2012; Kuhler et al., 1996) This is necessary and effective for eliminating the activation enthalpy error caused by the standard scale factors and the results were list in [Table S1](#)
105 and [Table S2](#), [Supplement](#). This was obtained by equation (1),

$$\lambda^{SRP,ZPE} = \lambda^{Anh} \lambda^H \quad (1)$$

where λ^{Anh} is the ratio of anharmonic zero-point vibrational energies (ZPE) to harmonic ZPE at the MPW1K/6-311+G(2df, 2p) level. λ^H is 0.983 for M06-2X/MG3S to correct harmonic frequencies. The result shows that the specific reaction scale factors are 0.955 for TS1 (See Table S1) and 0.956 for TS2 (See Table S1), which is a large deviation from the standard value
110 of 0.970; this results in a decrease in calculated enthalpies of activation of 0.72 and 0.78 for TS1 and TS2 at 0 K, respectively. In addition, multi-structural torsional anharmonicity involving reactant and transition state were all calculated using MS-T method (multi-structural method for torsional anharmonicity).(Yu et al., 2012; Zheng et al., 2011; Zheng and Truhlar, 2013)

2.3 kinetics calculations

The dual-level strategy was utilized to compute the high-pressure limit rate constant.(Long et al., 2016, 2019; Xia et al.,
115 2024) As shown in equation (2), we integrated a conventional transition-state theory rate constant k_{TST}^{HL} predicated on higher-level (HL, CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S) inputs with transmission coefficients derived from direct dynamics at a lower level (LL, M11-L/MG3S), employing a specific density functional that is chose from the results of benchmark calculations ([see Table S3](#)). We have incorporated both a recrossing transmission coefficient $\Gamma_{CVT/TST}^{LL}$ and a tunneling transmission coefficient k_{SCT}^{LL} , as calculated through reaction-path variational transition state theory, with a particular emphasis
120 on the canonical variational theory coupled with small-curvature tunneling (CVT/SCT).(Garrett and Truhlar, 1979; Liu et al., 1993; Truhlar et al., 1982) Additionally, a multi-structural transmission coefficient (F^{MS-T}) was introduced to this framework to cancel the errors caused by the multi-structural anharmonicity, thereby advancing our approach to the DL-MS-CVT/SCT method, which provides a detailed and multifaceted treatment of the rate constant calculation, and can effectively obtain quantitative kinetics.

$$k_{MS-CVT/SCT}^{DL} = F^{MS-T} \times k_{TST}^{HL} \times k_{SCT}^{LL} \times \Gamma_{CVT/TST}^{LL} \quad (2)$$

The pressure-dependent rate constants were done by employing the system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory in the temperature range of 190-350 K.(Bao et al., 2016b, a; Bao and Truhlar, 2017) This method relies only on the high-pressure limiting rate constant that was calculated by the dual-level strategy. The computational details of pressure-dependent rate constants are presented in the Supplement.

2.4 Atmospheric modelling

We used GEOS-Chem 14.4.2 with a horizontal resolution of $2.0^\circ \times 2.5^\circ$ to simulate space distribution of HO₂ and OH at 47 vertical layers in the period from February 2018 to February 2019.(Bey et al., 2001) The time includes six months of spin-up and output per hour. GEOS-Chem is a global, three-dimensional chemical transport model associated with atmospheric composition (<http://geos-chem.org>). Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2)(Gelaro et al., 2017) was used as meteorological field data and Harmonized Emissions Component (HEMCO 3.9) was used as the source of emissions data.(Lin et al., 2021) The emissions include biogenic emissions from Model of Emissions of Gases and Aerosols from Nature (MEGANv2.1)(Hu et al., 2015; McDuffie et al., 2020) and anthropogenic emissions from the global Community Emissions Data System (CEDS) (McDuffie et al., 2020) inventory. Simulation uses default full chemistry mechanism including HO_x-NO_x-VOC-O₃-halogen chemistry, which is done by our previous investigation.(Bloss et al., 2007)

2.5 Software

All density function calculation, including Zero-point energy (ZPE) correction were carried out using Gaussian 16 software package,(Zhao and Truhlar, 2008b) and the single point energy calculations for CCSD(T)-F12a/cc-pVTZ-F12 and FNO-CCSD(T)-F12a/cc-pVDZ-F12 were done using Molpro 2019(Werner et al., 2019) and MRCC code.(Kállay et al., 2020; M. Kállay, P. R. Nagy, D. Mester, L. Gyevi-Nagy, J. Csóka, P. B. Szabó, Z. Rolik, G. Samu, J. Csontos, B. Hégyely, Á. Ganyecz, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P. D. Mezei, 2022) MS-T method was executed through MSTor-2023 program package.(Chen et al., 2023) The rate constants were done with the KiSThelP,(Canneaux et al., 2014) Polyrate 2017-C, and Gaussrate 2017-B.(Zheng et al., 2017, n.d.)

3. Results and discussion

3.1. The electronic structure of the C₂F₅CHO/C₃F₇CHO + HO₂ reaction

We considered the C₂F₅CHO/C₃F₇CHO + HO₂ reaction similar to the reactions of aldehydes with HO₂.(Long et al., 2022) The dominant mechanism is that the hydrogen atom of HO₂ is transferred to the terminal oxygen atom of C₂F₅CHO/C₃F₇CHO, and simultaneously, the oxygen atom of HO₂ is connected to carbon atom of carbonyl group of C₂F₅CHO/C₃F₇CHO. [Figure 1](#)

depicts ZPE corrected potential energy profile of the reaction of $\text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO} + \text{HO}_2$ at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level. $\text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO}$ and HO_2 form reaction complexes RC1/RC2, and then pass through transition

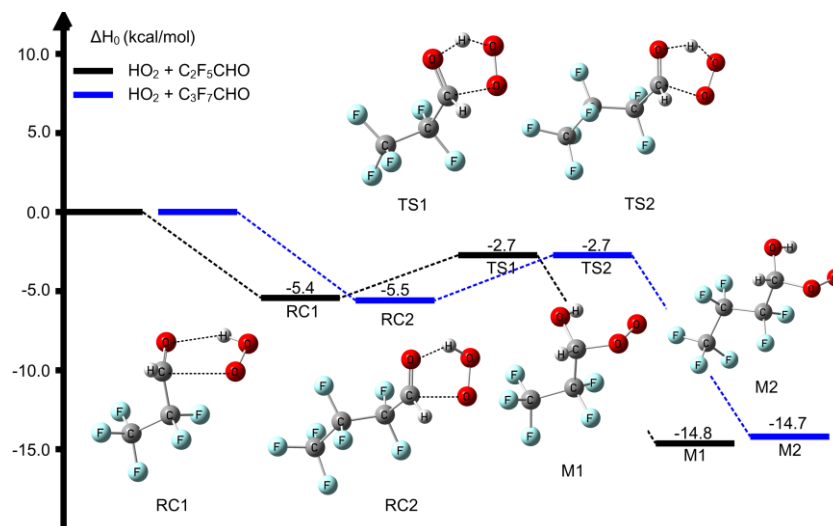


Figure 1. Enthalpy profile of the HO_2 addition reaction with $\text{C}_2\text{F}_5\text{CHO}$ and $\text{C}_3\text{F}_7\text{CHO}$ as calculated by CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level with the scale factor by the standard method at 0 K.

states TS1 and TS2 to form the intermediate products of $\text{C}_2\text{F}_5\text{CH}(\text{OH})\text{OO}$ (M1) and $\text{C}_3\text{F}_7\text{CH}(\text{OH})\text{OO}$ (M2), respectively. TS1 (-2.7 kcal/mol) denotes the global minimum optimized structures of the stationary points of enthalpy of activation at 0 K; this is 0.3 kcal/mol and 1.6 kcal/mol lower than that of the $\text{CF}_3\text{CHO} + \text{HO}_2$ and $\text{CH}_3\text{CHO} + \text{HO}_2$ reactions, respectively. (Long et al., 2022) This shows that the reaction of perfluoroaldehydes with HO_2 may be kinetically feasible. As a comparison, the further energy profile of the $\text{C}_3\text{H}_7\text{CHO} + \text{HO}_2$ reaction shows an equal enthalpy of activation of -2.7 kcal/mol for TS2; this is slightly lower than that of enthalpy of activation -2.4 kcal/mol for the reaction of $\text{CF}_3\text{CHO} + \text{HO}_2$. (Gao et al., 2024b)

It is noteworthy that Figure 1 only depicts the potential energy profile of the reaction featuring the global minimum structure. Nevertheless, the internal rotation of the C–C bond produces multiple conformers for reactants, transition states, and formed intermediate products. Their geometric configurations and energy distributions relative to the global minimum structure are presented in Figure S1. Regarding the reactions of $\text{C}_2\text{H}_5\text{CHO}$ and $\text{C}_3\text{H}_7\text{CHO}$ with HO_2 , we have observed that as the carbon chain lengthens, the number of conformers of both reactants and transition states increases, and the energy distribution broadens. For instance, TS1 has three isomers, with an energy distribution spanning from 0 to 1.7 kcal/mol, whereas TS2 has five isomers, and its energy distribution ranges from 0 to 1.9 kcal/mol. In terms of geometric configurations, the low-energy isomers tend to have more linear structures, while the high-energy conformations exhibit more pronounced curling.

NO is a highly reactive gas. (Lee et al., 2024) Human activities, especially agriculture and industrial processes, have led to significant NO emissions. (Andersen et al., 2024; Thomson et al., 2012) Industrial activities contribute to NO levels such as fossil fuel combustion in power plants and chemical manufacturing, along with vehicle emissions. Given its prevalence from human-induced emissions, we further explore the degradation pathways of intermediate products M1 and M2 in the presence

of NO. 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. Additionally, the formed intermediate products (M1 and M2) are a typical class of RO_2 radicals. In the low NO_x levels, these RO_2 radicals can also participate in bimolecular reactions. (Ding and Long, 2022) RO_2 can react with HO_2 , resulting in the formation of the stable product $ROOH$. Moreover, RO_2 can react with other RO_2 or $R'O_2$ (where R' denotes a hydrocarbon fragment). (Bottorff et al., 2023) The reaction with $R'O_2$ frequently yields alkoxy radicals, and both of these reactions are capable of producing stable products. (Goldman et al., 2021) Due to the complexity of these bimolecular reactions of the formed RO_2 in the reactions R1 and R2, we did not further investigate their reaction mechanisms and kinetics in the present work.

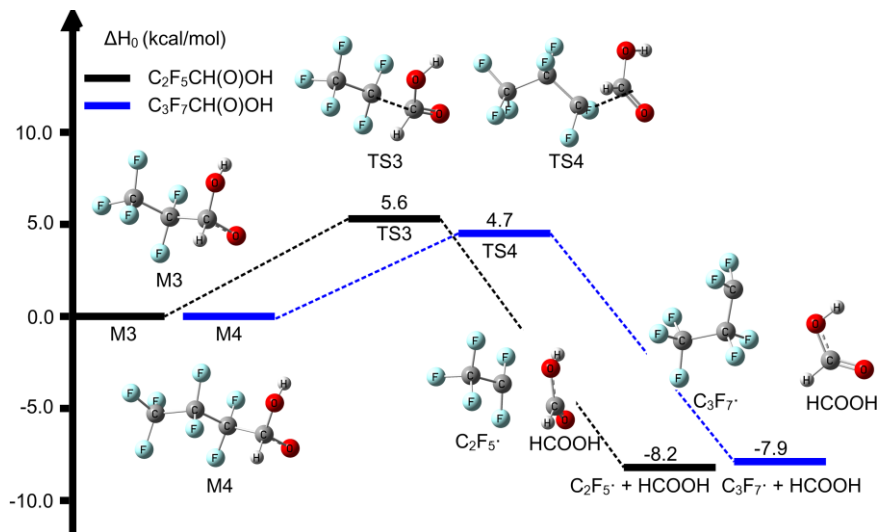


Figure 2. Relative enthalpies at 0 K for the decomposition of $C_2F_5CH(O)OH$ (M3) and $C_3F_7CH(O)OH$ (M4) calculated by CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S.

We further conducted an extended study on the reactions of C_4F_9CHO and $C_5F_{11}CHO$ at the FNO-CCSD(T)-F12//cc-pVDZ-F12//M06-2X/MG3S level, 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. Data from Figure 3 reveal an interesting phenomenon that the activation enthalpy at 0 K remains almost equal C2 (C_2F_5CHO) to C5 ($C_5F_{11}CHO$). This

finding aligns with the similar trend for the reaction of $C_nH_{2n+1}CHO$ with HO_2 , suggesting that the impact of carbon chain length growth on the enthalpy of activation at 0 K is quite minor. (Ding and Long, 2022; Gao et al., 2024b) However, the introduction of CF_3 leads to a relatively lower enthalpy of activation at 0 K for the $C_nH_{2n+1}CHO + HO_2$ reactions, primarily due to the strong electron-withdrawing ability of fluorine atoms, which can stabilize the transition

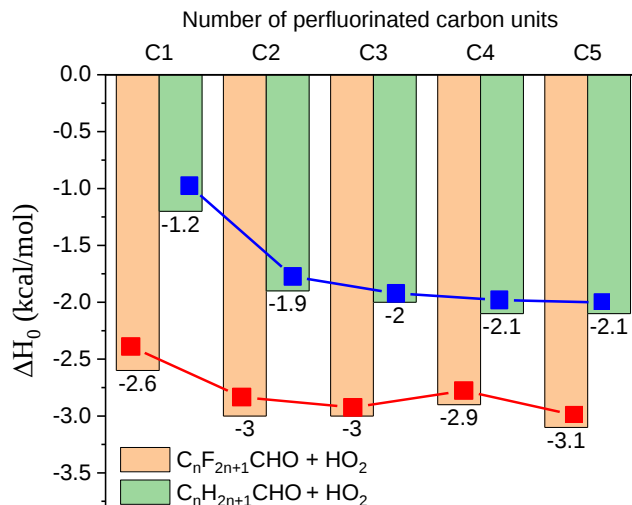


Figure 3. The impacts of perfluorinated carbon length on the enthalpies of activation at 0 K in the $C_nH_{2n+1}CHO/C_nF_{2n+1}CHO + HO_2$ reactions. The values for $C_nH_{2n+1}CHO$ ($n = 1-5$) + HO_2 and $C_nF_{2n+1}CHO + HO_2$ are obtained from references (Ding and Long, 2022; Gao et al., 2024a) and calculated by using FNO-CCSD(T)-F12a/cc-pVDZ-F12.

state and lower the enthalpy of activation at 0 K. As the size of perfluoroaldehyde increases, the multi-structure effects caused by torsion of C-C bonds become more pronounced. The relative energy values of reactants and transition states shown in Figure S1 and S3 (relative to the global minimum energy value, without ZPE correction) indicate that with increasing molecular size, the number of possible isomers increases, leading to a broader energy distribution. 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. This broad energy distribution has significant implications for the thermodynamics and kinetics of the degradation process of perfluoroaldehydes, potentially increasing the diversity and complexity of reaction pathways.

3.2. Kinetics of $C_2F_5CHO/C_3F_7CHO + HO_2$

The high-pressure limiting rate constants were calculated for the temperature range of 190–350 K, covering a wide atmospheric temperature range. For the reactions $C_2F_5CHO + HO_2$ (R1) and $C_3F_7CHO + HO_2$ (R2), the rate constants incorporating multi-structure anharmonicity corrections are defined as k_1 and k_2 , respectively. According to Zheng (Zheng and Truhlar, 2010), the rate constants at high pressure are fitted using equation (3).

$$k = A \left(\frac{T+T_0}{300} \right)^n \exp \left[-\frac{E(T+T_0)}{R(T^2 + T_0^2)} \right] \quad (3)$$

Table S4 lists the fitting parameters A, n, E, and T₀. Here, T represents temperature in Kelvin, and R is the ideal gas constant (0.0019872 kcal mol⁻¹ K⁻¹). The temperature-dependent Arrhenius activation energies are determined from the fits using equation (4).

$$E_0 = -R \frac{d \ln k}{d(1/T)} \quad (4)$$

The high-pressure limit rate constants, incorporating multiple-structure anharmonicity torsional corrections, are illustrated in Figure 4, with more comprehensive data provided in Tables S5-S7. Regarding the C₂F₅CHO + HO₂ reaction, the rate constant k_1 exhibits a decrease from 3.35×10^{-12} cm³ molecule⁻¹ s⁻¹ at 190 K to 5.42×10^{-14} cm³ molecule⁻¹ s⁻¹ at 350 K in Figure 4 and Tables S5-S7. Similarly, the rate constant k_2 for the C₃F₇CHO + HO₂ reaction also decreases with increasing temperature. These trends are consistent with theoretical studies of non-fluorinated aldehydes such as C₂H₅CHO and C₃H₇CHO, where rate constants for reactions with HO₂ were reported in the range of 10⁻¹⁴ to 10⁻¹³ cm³ molecule⁻¹ s⁻¹ at atmospheric temperatures, indicating similar reactivity between fluorinated and non-fluorinated aldehydes with HO₂. (Ding and Long, 2022; Gao et al., 2024a)

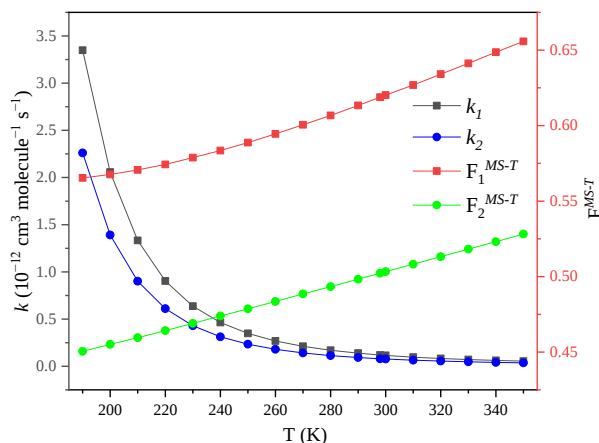


Figure 4. The high-pressure limit rate constants of the reactions of C₂F₅CHO and C₃F₇CHO with HO₂ at the temperature range of 190–350 K.

In addition, the effects of recrossing and multi-structural anharmonicity are quite limited, approximately ranging between 0.4 and 0.7 times. This results in the rate constants for reactions R1 and R2 being 2-3 times slower than that of CF₃CHO + HO₂. For instance, the rate constants of C₂F₅CHO + HO₂ and C₃F₇CHO + HO₂ are estimated to be 1.19×10^{-13} and 7.92×10^{-14} cm³ molecule⁻¹ s⁻¹ at 298 K, respectively, which is slow by compared to 2.48×10^{-13} cm³ molecule⁻¹ s⁻¹ of CF₃CHO + HO₂. (Long et al., 2022) Moreover, the effect of anharmonicity in vibrational-frequency scale factors on high pressure limited rate constants were further discussed. We define “ f ” as the ratio between the rate constant calculated using the reaction-specific vibrational-frequency scale factors and that calculated using the standard vibrational-frequency scale factors. As depicted in Figure 5, the

rate constants obtained using the reaction-specific scale factors are 3-7 and 4-10 times fast compared to those calculated using the standard scale factors. Consequently, employing reaction-specific scale factors is crucial for accurate rate calculations.

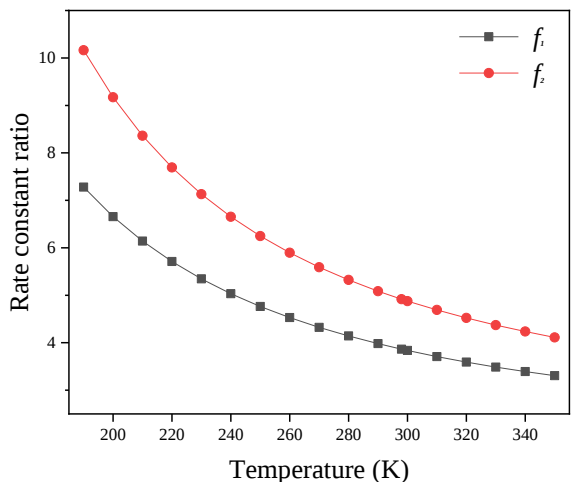


Figure 5. The ratio between the rate constant calculated using the reaction-specific vibrational-frequency scale factors and the rate constant calculated using the standard vibrational-frequency scale factors, within the temperature range of 190–350 K. f_1 and f_2 represent the ratios for the reactions of $\text{C}_2\text{F}_5\text{CHO} + \text{HO}_2$ and $\text{C}_3\text{F}_7\text{CHO} + \text{HO}_2$, respectively.

The pressure-dependent rate constants of the HO_2 reaction with $\text{C}_2\text{F}_5\text{CHO}$ and $\text{C}_3\text{F}_7\text{CHO}$ were further calculated by using SS-QRRK method. As shown in Figure 6-7 and Table S8-S9, it can be observed that variations of the calculated rate constant with respect to pressure have a minimal impact on the rate constant of $\text{C}_2\text{F}_5\text{CHO} + \text{HO}_2$, indicating the absence of significant pressure effects. However, significant pressure effects are observed in the $\text{C}_3\text{F}_7\text{CHO} + \text{HO}_2$ reaction, particularly at temperatures above 300 K. To provide a clearer perspective, we define the transition pressure $p_{1/2}$ to quantify the pressure dependence. Specifically, the transition pressure $p_{1/2}$ is the pressure at which the pressure-dependent rate constant reaches half of its high-pressure limit. Figure 8 and Table S10 show that the transition pressure $p_{1/2}$ for the $\text{HO}_2 + \text{C}_2\text{F}_5\text{CHO}$ reaction ranging from 2.6×10^{-5} to 7.4×10^{-3} bar at 190-350 K, while the transition pressure $p_{1/2}$ ranges from 2.6×10^{-2} to 2.3 bar at 190-350 K for the $\text{HO}_2 + \text{C}_3\text{F}_7\text{CHO}$ reaction. This indicates that the $\text{HO}_2 + \text{C}_3\text{F}_7\text{CHO}$ reaction exhibits a significant pressure dependence, and the increase in carbon chain length has a significantly affect pressure-dependent rate constants.

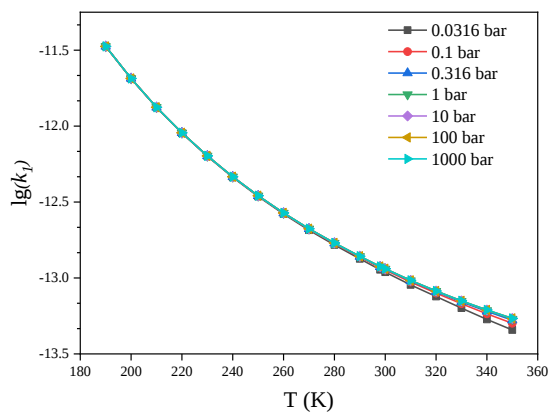


Figure 6. Pressure-dependent rate constants of $\text{C}_2\text{F}_5\text{CHO} + \text{HO}_2$ as functions of temperature obtained via the SS-QRRK method.

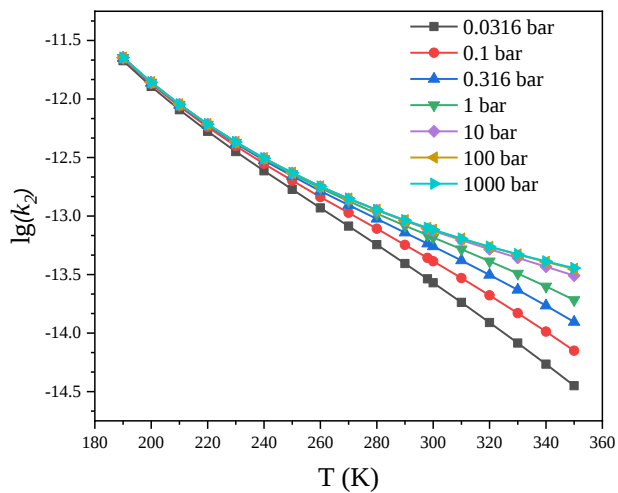
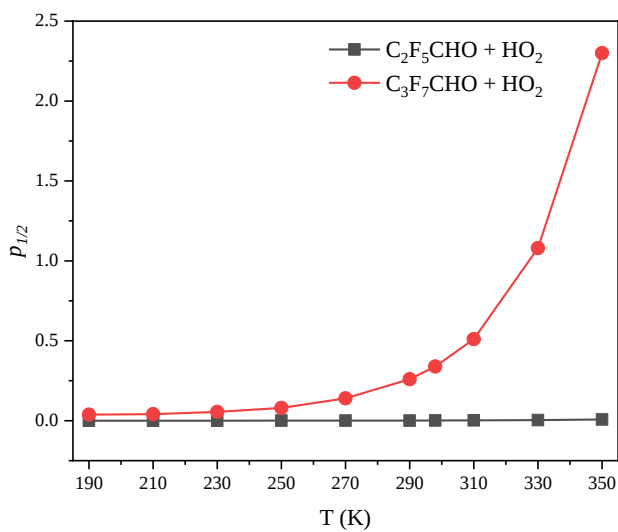


Figure 7. Pressure-dependent rate constants of $\text{C}_3\text{F}_7\text{CHO} + \text{HO}_2$ as functions of temperature obtained via the SS-QRRK method.



265 **Figure 8.** Transition pressure $p_{1/2}$ calculated by the SS-QRRK method for the $\text{HO}_2 + \text{C}_2\text{F}_5\text{CHO}$ and $\text{HO}_2 + \text{C}_3\text{F}_7\text{CHO}$ reactions as functions of temperature.

3.3. Atmospheric Implications.

Given that the reaction of $\text{OH} + \text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO}$ was considered to be the main sink for $\text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO}$, it is necessary to establish the competitive relationship between $\text{OH} + \text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO}$ and $\text{HO}_2 + \text{C}_2\text{F}_5\text{CHO}/\text{C}_3\text{F}_7\text{CHO}$.
 270 Therefore, we have defined the ratio of rate between them according to the equations (5) and (6).

$$v_1 = \frac{k_1[\text{C}_2\text{F}_5\text{CHO}][\text{HO}_2]}{k_{\text{OH}}[\text{C}_2\text{F}_5\text{CHO}][\text{OH}]} \tag{5}$$

$$v_2 = \frac{k_2[\text{C}_3\text{F}_7\text{CHO}][\text{HO}_2]}{k'_{\text{OH}}[\text{C}_3\text{F}_7\text{CHO}][\text{OH}]} \tag{6}$$

Here, k_1 and k_2 are the rate constants of $\text{HO}_2 + \text{C}_2\text{F}_5\text{CHO}$ and $\text{HO}_2 + \text{C}_3\text{F}_7\text{CHO}$ calculated by this work, respectively, while k_{OH} and k'_{OH} are the corresponding rate constants of $\text{OH} + \text{C}_2\text{F}_5\text{CHO}$ and $\text{OH} + \text{C}_3\text{F}_7\text{CHO}$, from the literature (Solignac et al.,
 275 2007; Wang et al., 2007). We calculated the rate ratios using a high OH concentration(Lew et al., 2020) of 5×10^6 molecules cm^{-3} and a typical HO_2 concentration(Brasseur and Solomon, 2006) of 1.4×10^8 molecules cm^{-3} . The calculations presented in Table 1 reveal that within the temperature range of 240-350 K, the rate ratios for v_1 and v_2 are in the

Table 1. Rate ratios of $\text{HO}_2 + \text{C}_2\text{F}_5\text{CHO}$ to $\text{OH} + \text{C}_2\text{F}_5\text{CHO}$ and $\text{HO}_2 + \text{C}_3\text{F}_7\text{CHO}$ to $\text{OH} + \text{C}_3\text{F}_7\text{CHO}$ within the Temperature Range of 240 to 350 K.

T(K)	k_{OH}^a	k'_{OH}^a	v_1^b	v_2^b
240	3.80×10^{-13}	4.30×10^{-13}	34.22	20.34
250	4.10×10^{-13}	4.57×10^{-13}	23.80	14.31
260	4.40×10^{-13}	4.84×10^{-13}	17.09	10.38
270	4.69×10^{-13}	5.10×10^{-13}	12.6	7.74
280	4.99×10^{-13}	5.35×10^{-13}	9.55	5.90
290	5.28×10^{-13}	5.60×10^{-13}	7.36	4.60
298	5.51×10^{-13}	5.80×10^{-13}	6.06	3.83
310	5.84×10^{-13}	6.08×10^{-13}	4.62	2.96
320	6.12×10^{-13}	6.31×10^{-13}	3.76	2.43
330	6.39×10^{-13}	6.54×10^{-13}	3.10	2.02
340	6.66×10^{-13}	6.76×10^{-13}	2.59	1.70
350	6.92×10^{-13}	6.97×10^{-13}	2.19	1.45

280 ^a k_{OH} and k'_{OH} are the rate constants of the OH reactions with $\text{C}_2\text{F}_5\text{CHO}$ and $\text{C}_3\text{F}_7\text{CHO}$, from the literature(Antiñolo et al., 2014; Solignac et al., 2007) respectively. ^b v_1 and v_2 denote the rate ratios of HO_2 with $\text{C}_2\text{F}_5\text{CHO}$ and $\text{C}_3\text{F}_7\text{CHO}$ to OH with $\text{C}_2\text{F}_5\text{CHO}$ and $\text{C}_3\text{F}_7\text{CHO}$, respectively.

range of 34.22 to 2.19 and 20.34 to 1.45, respectively. These substantial findings indicate that the reactions of HO₂ with C₂F₅CHO and C₃F₇CHO can dominate the removal of these compounds, comparing with the corresponding OH reactions, thereby exerting a substantial impact on their elimination processes. We also determined the rate constants governing the reactions of C₂F₅CHO and C₃F₇CHO with HO₂ within the altitude range of 0-50 km, and subsequently evaluated the atmospheric lifetimes of these compounds. The HO₂-mediated elimination pathways for C₂F₅CHO and C₃F₇CHO are characterized by relatively rapid reaction rates within the troposphere (< 10 km), resulting in relatively short atmospheric lifetimes of approximately 14.4 - 31.3 hours and 21.6 - 51.8 hours (See Table 2). These atmospheric lifetimes are considerably shorter than the 20-day atmospheric lifetime estimated for the reactions involving OH radicals with C₂F₅CHO and C₃F₇CHO, and even can somewhat shorter than photolysis (one day)(Solignac et al., 2007). This highlights the noteworthy impact of HO₂-initiated elimination pathways on the atmospheric degradation of these compounds.

Table 2. Hydroperoxyl radical concentration (in molecules cm⁻³), rate constants (in cm³ 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	<i>k</i> ₁ (T, <i>p</i>) ^c	<i>k</i> ₂ (T, <i>p</i>) ^c	τ ₁ ^d	τ ₂ ^d
0	290.2	1010	1.40E+08	1.38E-13	9.18E-14	1.44E+01	2.16E+01
5	250.5	496	4.90E+07	3.44E-13	2.30E-13	1.65E+01	2.47E+01
10	215.6	243	8.30E+06	1.07E-12	6.47E-13	3.13E+01	5.18E+01
15	198	119	2.30E+06	2.21E-12	2.98E-13	5.47E+01	4.05E+02
20	208	58.2	2.90E+06	1.38E-12	1.22E-13	6.93E+01	7.85E+02
25	216.1	28.5	5.70E+06	9.38E-13	4.32E-14	5.20E+01	1.13E+03
30	221.5	13.9	7.50E+06	6.52E-13	1.29E-14	5.68E+01	2.88E+03
35	228.1	6.83	6.90E+06	4.04E-13	4.13E-15	9.96E+01	9.74E+03
40	240.5	3.34	5.90E+06	2.29E-13	1.73E-15	2.06E+02	2.73E+04
45	251.9	1.64	4.90E+06	1.27E-13	6.56E-16	4.45E+02	8.64E+04
50	253.7	0.801	4.00E+06	5.87E-14	1.80E-16	1.18E+03	3.86E+05

^aH denotes altitude (atmospheric scale height); T denotes temperature; p denotes pressure. ^bData are from ref (Brasseur and Solomon, 2006). ^c*k*₁, *k*₂ are the rate constants of the HO₂ reactions with C₂F₅CHO and C₃F₇CHO, respectively. ^dτ₁ = 1/(*k*₁[HO₂]) and τ₂ = 1/(*k*₂[HO₂]) define the atmospheric lifetimes for HO₂ reactions with C₂F₅CHO and C₃F₇CHO, respectively.

To provide further insight into the importance of these reactions in the atmosphere, we analyse the concentrations of HO₂ and OH by using Geos-Chem. The concentration of modelled HO₂ reached a maximum of 4.99 × 10⁸ molecule cm⁻³ in the Amazon region and a mean value of 9.93 × 10⁷ molecule cm⁻³.(Long et al., 2024) Simultaneously, the concentrations of HO₂ (1.7 × 10⁷ molecule cm⁻³) is consistent with field observations at the British Antarctic Survey’s Halley Research Station (1.5 ppt).(Bloss et al., 2007) We also note that there is a maximum concentration of 8.03 × 10⁶ molecule cm⁻³ over the Atlantic and Pacific oceans and an average concentration of 1.06 × 10⁶ molecule cm⁻³ for OH.(Lelieveld et al., 2016) Based on the rate ratios calculated above, when the concentration of HO₂ is two orders of magnitude higher than that of OH, the reaction with

305 HO₂ dominates over the reaction with OH. Therefore, we compare HO₂ and OH concentrations in global regions and find at least a 2-order of magnitude difference in concentrations in industrial parks such as Russia, Malaysia, and parts of Africa (see Figure 9). Specifically, in parts of Africa, HO₂ concentrations are even three orders of magnitude higher than that of OH. Additionally, high HO₂/OH ratios have been observed along the Indian Ocean margin near Indonesia, which may be attributed to atmospheric transport and enhanced HO₂ production from industrial activities. In the Amazon region, the [HO₂]/[OH] ratio
310 can reach as high as 410–1,200. This significantly increases the HO₂-to-OH degradation rate ratios for C₂F₅CHO and C₃F₇CHO, reaching 88.5–259 and 56.0–164, respectively. These rate ratios indicate that HO₂-driven degradation exceeds OH-mediated degradation by over 50 times. This large concentration ratios between HO₂ and OH suggests that HO₂ leads to sink of C₂F₅CHO and C₃H₇CHO at night in these regions. In contrast, over oceanic regions like the Atlantic and Pacific, the [HO₂]/[OH] ratios drop below 1, leading to a diminished role of HO₂ in these areas.

315 Our further analysis of the global distribution of the ratio between HO₂ and OH during daytime reveals that HO₂ 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 HO₂ is significantly higher than that of OH, which may be related to local industrial activities
320 or specific emission characteristics. However, due to the presence of daytime photolysis, the generation and loss pathways of HO₂ and OH become more complex, leading to significant uncertainty in interpreting the ratio. For instance, photolysis can alter the formation rates of HO₂ 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, HO₂ may play a role in the oxidation pathways of
325 C₂F₅CHO and C₃H₇CHO 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 HO₂/OH ratio.

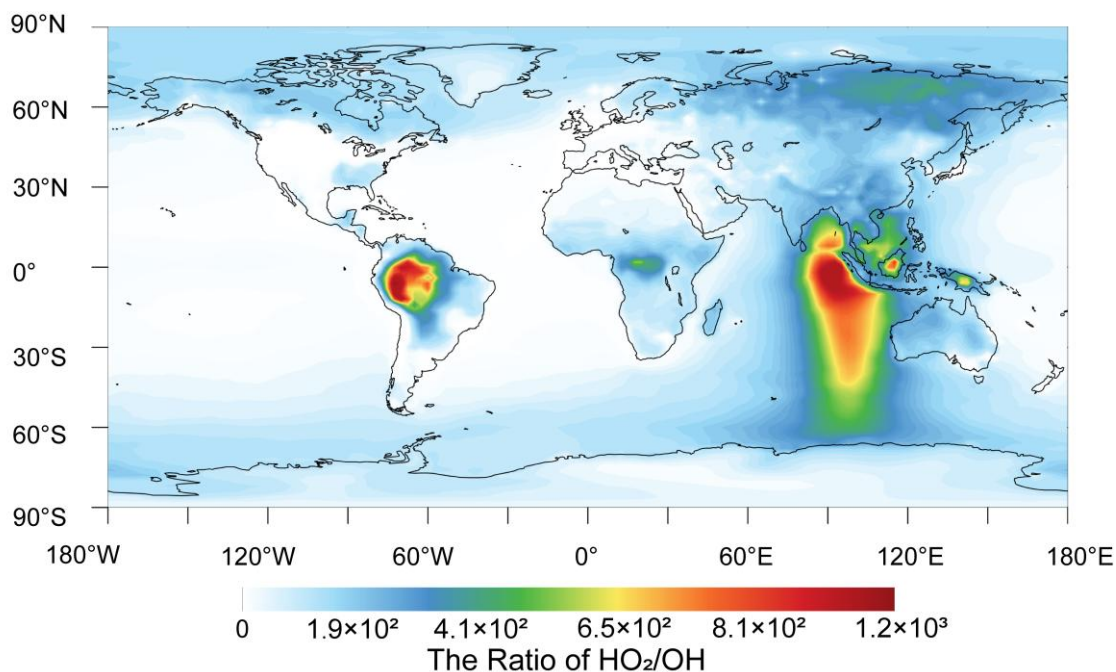


Figure 9. The annual average ratio of HO_2/OH at night globally.

Moreover, except for generating formic acid, another intermediate product $\text{C}_n\text{F}_{2n+1}$ can undergo a single-carbon shortening process as depicted in Figure 10 to ultimately convert into the more stable COF_2 . Taking the example of C_2F_5 , the process starts with C_2F_5 reacting with O_2 to form $\text{C}_2\text{F}_5\text{O}_2$. Subsequently, $\text{C}_2\text{F}_5\text{O}_2$ reacts with NO to produce $\text{C}_2\text{F}_5\text{O}$, 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 $\text{RO}_2 + \text{NO}$ reactions (e.g., $\text{M1/M2} + \text{NO}$) into atmospheric models, which is beyond the scope of this study.

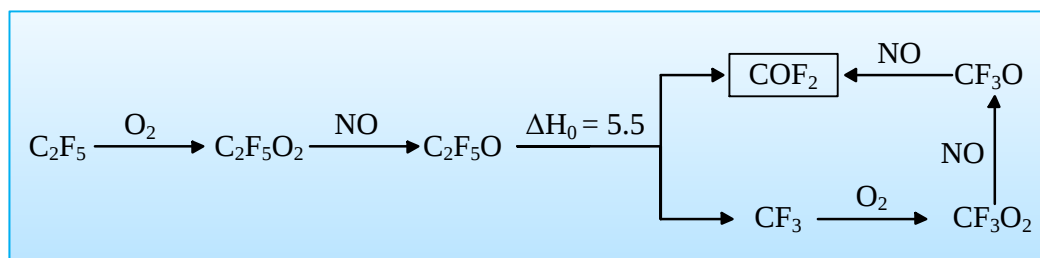


Figure 10. Atmospheric degradation mechanism for $\text{C}_n\text{F}_{2n+1}$ with C_2F_5 used as a representative example.

In current studies, we focus on the homogeneous reactions of HO_2 -initiated linear perfluoroaldehydes. It is worth noting that the concentration of HO_2 at interfaces may be higher than in the gas phase, according to research findings. (Angelaki et al., 2024; Li et al., 2023) Given the strong reactivity at the water-air interface and the complex interplay and competition between

OH and HO₂, the degradation of perfluoroaldehydes initiated by HO₂ and their potential contribution to atmospheric acidity may have a more pronounced impact. For example, Xia et al. (2024) recently reported the single-carbon and double-carbon pathways presented during the degradation of C₇F₁₅ on the surface of water droplets. These heterogeneous reactions may also contribute to the removal of perfluoroaldehydes and the degradation process of polyfluoroalkyl substances. Nevertheless, further kinetics and mechanism are still required as a basis and support, so as to enable a more accurate and comprehensive understanding of this complex chemical process and its impact on atmospheric chemistry.

4. Summarizing Remarks

In this study, we have delved into the chemical reaction kinetics of linear perfluorinated aldehydes (C₂F₅CHO and C₃F₇CHO) with hydroperoxyl radicals in the gas phase using ab initio calculation methods and reaction kinetics theory. We find that the activation enthalpies for the reactions of C₂F₅CHO and C₃F₇CHO with HO₂ 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 C₄F₉CHO and C₅F₁₁CHO with HO₂. Further kinetic studies reveal that anharmonicity have a significant impact on the reaction rates, while the torsional anharmonicity, recross coefficient, and tunnelling effects contribute relatively little to the rate constants. It is particularly noteworthy that the reaction of C₃F₇CHO with HO₂ exhibits a distinct pressure dependence, whereas the reaction of C₂F₅CHO with HO₂ does not show such a pressure effect.

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 HO₂ concentration exceeds OH concentration by 2–3 orders of magnitude. Therefore, the reactions of HO₂ with C₂F₅CHO and C₃F₇CHO can compete well with their corresponding reaction with OH. Specifically, the atmospheric lifetimes of C₂F₅CHO and C₃F₇CHO via HO₂ 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 COF₂ formation.

While the present investigation establishes the HO₂-mediated degradation pathway for linear perfluoroaldehydes (C₂F₅CHO/C₃F₇CHO), it simultaneously highlights critical gaps in our understanding of their atmospheric lifetimes. Notably, the current work focuses on gas-phase HO₂ reactions. However, the roles of heterogeneous interfacial processes (e.g., on aerosol surfaces or cloud droplets) remains unexplored. (Zhang et al., 2024b) The potential for HO₂-driven defluorination to generate reactive CF₃ radicals, which could initiate secondary reactions (e.g., with O₃ or NO₂), requires systematic investigation to assess implications for atmospheric oxidizing capacity and secondary aerosol formation. Additionally, the study focuses on radical-driven pathways but acknowledges that photolysis is a competing sink for linear perfluoroaldehydes. Future work should quantify photolysis rates under stratospheric UV conditions (e.g., 200–300 nm) to reconcile discrepancies between modeled and observed atmospheric lifetimes. (Thomson et al., 2025) Addressing these limitations will require integrating advanced experimental techniques (e.g., synchrotron-based photoionization mass spectrometry) with multi-scale modeling

frameworks, while prioritizing under sampled environments like the upper troposphere and polar regions where HO₂ reactivity anomalies could profoundly alter PFAS degradation trajectories.(Alam et al., 2024; Zhou et al., 2024b) Such efforts are critical for refining environmental risk assessments of emerging HFOs and guiding the design of next-generation chemicals with minimized atmospheric persistence.

Supplementary Material

Separate document

380 Author contributions.

BL designed the project; ZGD performed the quantum chemical calculations; CLX performed the model calculations; ZGD, CLX, and BL analysed the data; ZGD wrote the manuscript draft. ZGD, CLX, and BL reviewed and edited the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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