

Reactions of Carbonyl Oxide with Aldehydes: Accurate Electronic Structure Methods, Kinetic Insights, and Atmospheric Implications

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Abstract: Carbonyl oxide (CH₂OO) is paramount in atmospheric oxidation chemistry, yet quantitative kinetics data for its bimolecular reactions are very limited and even unknown. Here we establish a computational framework to obtain quantitative kinetics from small to large reaction systems. For CH₂OO + HCHO, we develop electronic structure methods to reach CCSDTQ/CBS accuracy for its activation enthalpies at 0 K. For CH₂OO + aldehydes (RCHO; R = CH₃-C₅H₁₁, CH₂F, CHF₂, CF₃), we introduce two strategies that recover CCSDTQ/CBS-quality activation enthalpies at 0 K. A dual-level strategy has been used to calculate their kinetics. The calculated rate constants show excellent agreement with available experimental data for CH₂OO + RCHO (R = CH₃-C₃H₇), which validates the designed computational framework. We find that fluorination leads to exceptional rate enhancement, with reactions of CHF₂CHO and CF₃CHO exceeding 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ over 200–320 K, approaching the collision limit. We also find that fluorination-driven reactivity enhancement originates predominantly from lower-level electronic effects than that of post-CCSD(T). Incorporation of the kinetics into a global chemical transport model uncovers previously unrecognized atmospheric impacts, with CH₂OO + HCHO reducing nighttime CH₂OO and gas-phase sulfate concentrations by 25.3% in Antarctica and 12.2% over Canada, respectively. The present findings address a long-term challenge in how to obtain quantitative kinetics for large molecular systems, where post-CCSD(T) calculations are prohibitive and provide new insights into the chemical transformation of CH₂OO and fluorinated aldehydes in the atmosphere.

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22 **1 Introduction**

23 Aldehydes are a major class of oxygenated volatile organic compounds (OVOCs) that substantially influence atmospheric
24 oxidative capacity, secondary organic aerosol (SOA) formation, and air quality (Lary and Shallcross, 2000; Liu et al., 2022;
25 Zhao et al., 2024; Li et al., 2024; Mellouki et al., 2015; Bao et al., 2025; Zhang et al., 2012; Bari and Kindzierski, 2018;
26 Edwards et al., 2014; Yang et al., 2018). They originate from both direct emissions—including biomass and fossil-fuel
27 combustion, biogenic sources, and vehicle exhaust—and secondary production via VOC oxidation (Zhao et al., 2024; Knote
28 et al., 2014; Parrish et al., 2012; Chen et al., 2014; Luecken et al., 2012; Grosjean et al., 1983). Their atmospheric removal is
29 governed primarily by photolysis and OH reactions during daytime, whereas fluorinated aldehydes exhibit notably reduced
30 OH reactivity (Wenger, 2006; Jiménez et al., 2007; Atkinson and Pitts, 1978; Lily et al., 2021; Sellevåg et al., 2005; Scollard
31 et al., 1993; Thévenet et al., 2000; D'anna et al., 2001). NO₃ reactions constitute a nighttime sink but proceed extremely slow,
32 highlighting the need to identify alternative nocturnal loss pathways (Cabañas et al., 2001; Bossmeyer et al., 2006; Papagni et
33 al., 2000).

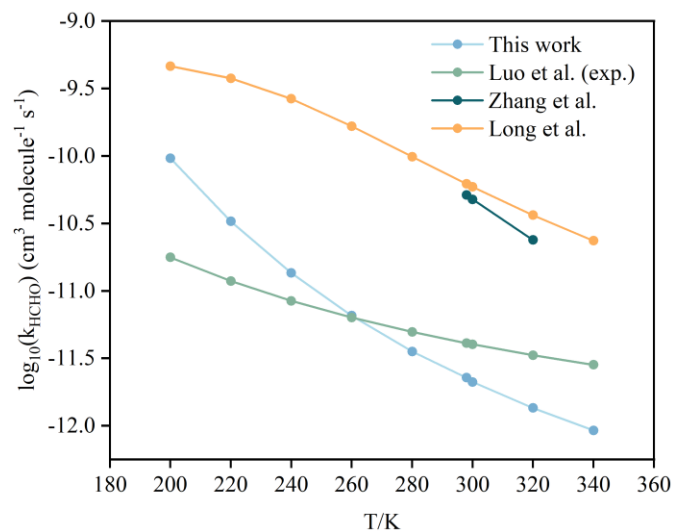
34 Stabilized Criegee intermediates (sCIs), key intermediate species of O₃-initiated alkene ozonolysis (Criegee, 1975;
35 Criegee and Wenner, 1949), play critical roles in atmospheric oxidation and SOA formation (Khan et al., 2018; Novelli et al.,
36 2014; Percival et al., 2013; Chhantyal-Pun et al., 2020) and react rapidly with acids (Cabezas and Endo, 2019; Chung et al.,
37 2019; Peltola et al., 2020; Foreman et al., 2016; Raghunath et al., 2017), amides (Wei et al., 2022; Long et al., 2025), and SO₂
38 (Berndt et al., 2014; Boy et al., 2013; Manonmani et al., 2023; Kukui et al., 2021). Accurate kinetics for their bimolecular
39 reactions are therefore essential for constraining their atmospheric fate.

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45 **Table 1.** Rate constants of CH₂OO + HCHO by previous investigation at different temperatures and pressures.

| Reaction | P (Torr) | T (K) | $k(T)$ (cm ³ molecule ⁻¹ s ⁻¹) | Ref. |
|----------|----------|------------------------|--|-----------------------|
| Exp. | 56 | 296 | $(4.11 \pm 0.25) \times 10^{-12}$ | (Luo et al., 2023) |
| | 78 | 275 | $(4.84 \pm 0.41) \times 10^{-12}$ | (Enders et al., 2024) |
| | | 295 | $(3.50 \pm 0.35) \times 10^{-12}$ | |
| Theory | 10 | 213 | 3.28×10^{-9} | (Zhang et al., 2023) |
| | 202 | 230 | 1.29×10^{-9} | |
| | 406 | 259 | 3.52×10^{-10} | |
| | 760 | 296 | 5.51×10^{-10} | |
| | | 295 | 5.71×10^{-10} | |
| | 296 | 6.52×10^{-11} | (Long et al., 2021) | |
| | 275 | 1.11×10^{-10} | | |
| | 295 | 6.68×10^{-11} | | |
| | 296 | 3.01×10^{-11} | This work | |
| | 275 | 5.62×10^{-11} | | |
| | 295 | 3.10×10^{-11} | | |

46 Despite numerous studies on CH₂OO + aldehydes, important gaps remain (Table 1 and Figure 1) for CH₂OO + HCHO,
 47 theoretical and experimental rate constants differ by an order of magnitude (Luo et al., 2023; Enders et al., 2024; Long et al.,
 48 2021; Zhang et al., 2023); prior work on CH₂OO + CH₃CHO/C₂H₅CHO/C₃H₇CHO (Tables 2-3) relied primarily on CCSD(T)
 49 despite evidence that higher-level excitations are required (Taatjes et al., 2012; Elsamra et al., 2016; Stone et al., 2014; Berndt
 50 et al., 2015; Jiang et al., 2024; Kaipara and Rajakumar, 2018; Liu et al., 2020; Liu et al., 2023; Cornwell et al., 2023; Debnath
 51 and Rajakumar, 2024); and key effects such as anharmonicity, torsional anharmonicity, and recrossing were generally neglected
 52 (Luo et al., 2023; Enders et al., 2024; Kaipara and Rajakumar, 2018; Debnath and Rajakumar, 2024; Jalan et al., 2013).



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Figure 1. A comparison of reported rate constants for the CH₂OO + HCHO reaction from previous studies at different temperatures and high-pressure limit.

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Table 2. Rate constants of CH₂OO + CH₃CHO by previous investigation at different temperatures and pressures.

| Reaction | P (Torr) | T (K) | $k(T)$ (cm ³ molecule ⁻¹ s ⁻¹) | Ref. |
|----------|-----------------------------------|------------------------------------|--|------------------------|
| Exp. | 4 | 293 | $(9.50 \pm 0.70) \times 10^{-13}$ | (Taatjes et al., 2012) |
| | 25 | 298 | $(1.20 \pm 0.20) \times 10^{-12}$ | (Elsamra et al., 2016) |
| | | 340 | $(8.00 \pm 1.10) \times 10^{-13}$ | |
| | 4 | 298 | $(1.10 \pm 0.10) \times 10^{-12}$ | |
| | 50 | | $(1.30 \pm 0.20) \times 10^{-12}$ | |
| | 25 | 295 | $(1.48 \pm 0.04) \times 10^{-12}$ | (Stone et al., 2014) |
| | 760 | 297 | $(1.70 \pm 0.50) \times 10^{-12}$ | (Berndt et al., 2015) |
| | 78 | 275 | $(2.37 \pm 0.21) \times 10^{-12}$ | (Enders et al., 2024) |
| | | 295 | $(1.61 \pm 0.14) \times 10^{-12}$ | |
| | 50 | 280 | $(2.57 \pm 0.46) \times 10^{-12}$ | (Jiang et al., 2024) |
| | | 298 | $(2.13 \pm 0.38) \times 10^{-12}$ | |
| | 5.5 | 298 | $(1.73 \pm 0.32) \times 10^{-12}$ | |
| | 10 | | $(2.08 \pm 0.38) \times 10^{-12}$ | |
| | 30 | | $(2.10 \pm 0.38) \times 10^{-12}$ | |
| | 50 | | $(2.13 \pm 0.38) \times 10^{-12}$ | |
| 100 | $(2.16 \pm 0.38) \times 10^{-12}$ | | | |
| 80 | 275 | $(10.20 \pm 0.80) \times 10^{-13}$ | (Cornwell et al., 2023) | |

| | | | | |
|--------|-----|-----|-----------------------------------|-----------|
| | | 295 | $(8.00 \pm 0.70) \times 10^{-13}$ | |
| Theory | 760 | 275 | 4.63×10^{-12} | This work |
| | | 280 | 4.02×10^{-12} | |
| | | 293 | 2.83×10^{-12} | |
| | | 295 | 2.69×10^{-12} | |
| | | 297 | 2.56×10^{-12} | |
| | | 298 | 2.50×10^{-12} | |

58 Moreover, no kinetic data exist for reactions with larger or fluorinated aldehydes, including pentanal, hexanal, CH₂FCHO,
59 CHF₂CHO, and CF₃CHO. To address these gaps, atmospheric models have effectively utilized rate constants derived from
60 empirical structure–reactivity relationships (SRRs)—such as those proposed by Jenkin et al. (Jenkin et al., 2018)—which
61 provide a practical and robust framework for large-scale modeling. Given the inherent complexity of computing atmospheric
62 kinetics, these empirical methods remain a primary tool for estimation.

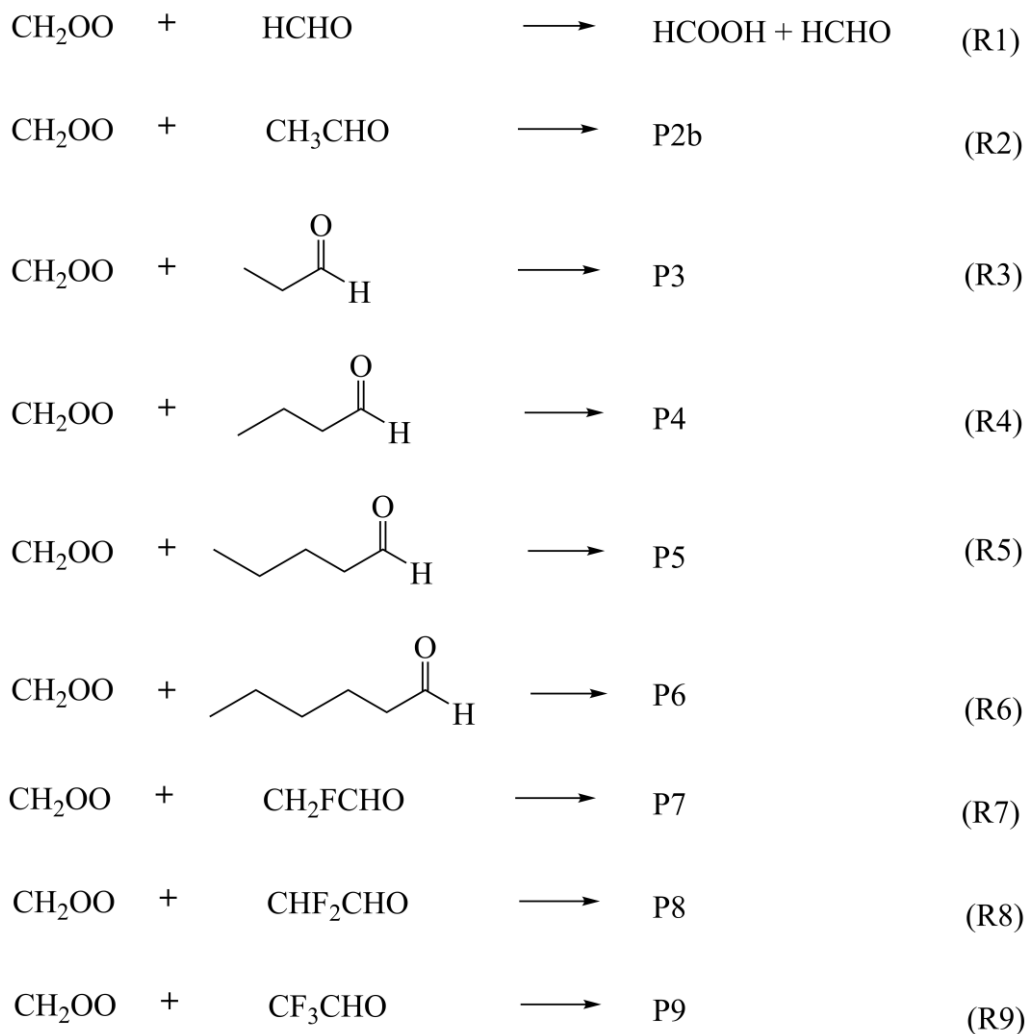
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64 **Table 3.** Rate constants of CH₂OO + RCHO (R = C₂H₅/C₃H₇) by previous investigation at different temperatures and pressures.

| Reaction | | P | T | $k(T)$ (cm ³ molecule ⁻¹ s ⁻¹) | Ref. | |
|-----------------------------------|---------|----------|-----------------------------------|--|------------------------|-------------------------------|
| C ₂ H ₅ CHO | Exp. | 50 Torr | 283 K | $(3.55 \pm 0.50) \times 10^{-12}$ | (Liu et al., 2020) | |
| | | | 298 K | $(3.12 \pm 0.44) \times 10^{-12}$ | | |
| | | 5 Torr | 298 K | $(2.39 \pm 0.22) \times 10^{-12}$ | | |
| | | 5.2 Torr | | $(2.52 \pm 0.24) \times 10^{-12}$ | | |
| | | 10 Torr | | $(3.07 \pm 0.20) \times 10^{-12}$ | | |
| | | 25 Torr | | $(2.12 \pm 0.19) \times 10^{-12}$ | | |
| | | 75 Torr | | $(3.30 \pm 0.20) \times 10^{-12}$ | | |
| | | 100 Torr | | $(3.08 \pm 0.19) \times 10^{-12}$ | | |
| | | 150 Torr | | $(3.18 \pm 0.19) \times 10^{-12}$ | | |
| | | 200 Torr | | $(3.19 \pm 0.21) \times 10^{-12}$ | | |
| | 78 Torr | 275 K | $(4.35 \pm 0.38) \times 10^{-12}$ | (Enders et al., 2024) | | |
| | | 295 K | $(3.29 \pm 0.29) \times 10^{-12}$ | | | |
| | Theory | HPL | | 283 K | 2.29×10^{-12} | (Kaipara and Rajakumar, 2018) |
| | | | | 298 K | 1.51×10^{-12} | |
| | | | | 275 K | 2.92×10^{-12} | |
| 295 K | | | | 1.63×10^{-12} | | |
| 283 K | | | | 4.49×10^{-12} | This work | |
| 298 K | | | | 3.11×10^{-12} | | |

| | | | | | |
|-----------------------------------|--------|---------|-------|-----------------------------------|-------------------------------|
| | | | 275 K | 5.57×10^{-12} | |
| | | | 295 K | 3.33×10^{-12} | |
| C ₃ H ₇ CHO | Exp. | 50 Torr | 253 K | $(4.20 \pm 0.10) \times 10^{-12}$ | (Debnath and Rajakumar, 2024) |
| | | | 268 K | $(3.61 \pm 0.10) \times 10^{-12}$ | |
| | | | 283 K | $(2.99 \pm 0.22) \times 10^{-12}$ | |
| | | | 298 K | $(2.63 \pm 0.14) \times 10^{-12}$ | |
| | Theory | HPL | 253 K | 8.83×10^{-12} | This work |
| | | | 268 K | 5.30×10^{-12} | |
| | | | 283 K | 3.38×10^{-12} | |
| | | | 298 K | 2.27×10^{-12} | |

65 Here, we investigate CH₂OO reactions with nine aldehydes (RCHO; R = H, CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, CH₂F, CHF₂,
66 CF₃) to obtain quantitative rate constants and to establish a general high-accuracy computational protocol applicable from
67 small benchmark systems to large atmospheric molecules. For the prototypical CH₂OO + HCHO reaction, we develop the
68 GMM(Q).L4 composite scheme that approaches full-CI accuracy, and for the broader reaction suite we devise a scalable
69 strategy capable of delivering near-full-CI activation energies. Dual-level strategy calculations accounting for all major
70 anharmonic and dynamical effects yield benchmark-quality rate constants, which are subsequently implemented in GEOS-
71 Chem to quantify their atmospheric impacts. This work provides a broadly extensible computational framework and
72 significantly advances the understanding of CH₂OO–aldehyde chemistry.



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74 **Scheme 1.** Reactions of CH₂OO with aldehydes75 **2 Computational methods and strategies**76 **2.1 Electronic structure best estimates for the CH₂OO + HCHO reaction**

77 Accurate electronic-structure data are essential for quantitative kinetics. All geometries and harmonic frequencies were
 78 optimized at the CCSD(T)-F12a/cc-pVTZ-F12 level (Adler et al., 2007; Knizia et al., 2009; Bischoff et al., 2009). To approach
 79 the full-CI limit for single-point energies, we developed a composite protocol, GMMQ.L4, which effectively reproduces

80 CCSDTQ/CBS quality:

$$81 \quad E_{\text{GMMQ.L4}} = E_{\text{MW2-F12.L}} + \Delta E_{\text{T-(T)}} + \Delta E_{\text{(Q)-T}} + \Delta E_{\text{Q-(Q)}} \quad (1)$$

82 Here, $E_{\text{MW2-F12.L}}$ is obtained from the previously validated MW2-F12.L scheme which detailed in Table S7 (Long et al.,
83 2021). $\Delta E_{\text{T-(T)}}$ (CCSDT-CCSD(T)) and $\Delta E_{\text{(Q)-T}}$ (CCSDT(Q)-CCSDT) are extrapolated to the CBS limit (cc-pVDZ \rightarrow cc-
84 pVTZ and cc-pVDZ \rightarrow VTZ(d)) using

$$85 \quad \Delta E_{\text{L}} = \Delta E_{\text{CBS}} + \frac{A}{L^3} \quad (2)$$

86 with $L=2$ for cc-pVDZ and 3 for cc-pVTZ and VTZ(d).

87 The final correction, $\Delta E_{\text{Q-(Q)}}$, is evaluated at the CCSDTQ-CCSDT(Q) level using the VDZ(NP) basis set. VTZ(d) employs
88 H(s) and heavy-atom(sp), while VDZ(NP) uses H(s) and heavy-atom(sp) functions (Chan and Radom, 2015).

89 Coupled-cluster theory converges systematically toward Full configuration interaction (Full-CI), but the steep scaling
90 necessitates truncation. Previous studies have established rapid basis-set convergence for both CCSDT(Q)-CCSDT and
91 CCSDT-CCSD(T) (Long et al., 2021; Long et al., 2019; Xia et al., 2025). Consistently, the CCSDTQ-CCSDT(Q) contribution
92 in our system is only 0.096 kcal mol⁻¹, indicating that excitations beyond quadruples contribute <0.10 kcal mol⁻¹ in Table S1.
93 Thus, GMMQ.L4//CCSD(T)-F12a/cc-pVTZ-F12 serves as the benchmark level in our dual-level kinetics framework.

94 We further compared GMMQ.L4 with the W3X-L composite method (Chan and Radom, 2015) for reaction R1. Although
95 both protocols include identical post-CCSD(T) contributions, GMMQ.L4 employs the MW2-F12.L component, whereas
96 W3X-L is based on W2X. Detailed comparisons are provided in Tables S1, S7, and S8. The observed deviation of 0.24 kcal
97 mol⁻¹ indicates that W3X-L does not achieve quantitatively reliable barrier heights for this system. Our analysis shows that
98 this discrepancy primarily originates from the difference between MW2-F12.L and W2X. Specifically, MW2-F12.L includes
99 HF energies, ΔCCSD and $\Delta(\text{T})$ correlation contributions, core-valence ($\Delta(\text{C+V})$) corrections, and scalar relativistic ($\Delta(\text{C+R})$)
100 effects, all evaluated with larger basis sets. In contrast, W2X comprises analogous HF, ΔCCSD , $\Delta(\text{T})$, and $\Delta(\text{C+R})$ terms, but
101 these are computed using smaller basis sets. The calculated results the difference of 0.24 kcal mol⁻¹ comes from the $\Delta(\text{C+V})$
102 and $\Delta(\text{C+R})$ terms, which differ by 0.19 kcal/mol and 0.12 kcal/mol, respectively. Additionally, CCSD(T)-F12 convergence

103 was verified by comparing W2X energies computed with cc-pVTZ-F12 and cc-pVDZ-F12 geometries; the difference of only
104 0.04 kcal mol⁻¹ confirms near-CBS performance of CCSD(T)-F12 for structural and vibrational data (See Table 4).

105 **Table 4.** Calculated enthalpies of activation at 0 K (ΔH_0^\ddagger in kcal/mol, relative to the bimolecular reactants) and unsigned
106 deviation (MUD) (in kcal/mol).

| Methods | ΔH_0^\ddagger | |
|-------------------------------------|-----------------------|------|
| | TS1 | UD |
| GMMQ.L4//CCSD(T)-F12a/cc-pVTZ-F12 | -4.97 | 0.00 |
| BE1//CCSD(T)-F12a/cc-pVTZ-F12 | -4.97 | 0.00 |
| BE2//CCSD(T)-F12a/cc-pVTZ-F12 | -4.97 | 0.00 |
| M11-L/MG3S | -5.16 | 0.19 |
| W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 | -5.22 | 0.24 |
| MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12 | -5.41 | 0.44 |
| W2X//DF-CCSD(T)-F12a/jun-cc-pVDZ | -5.60 | 0.63 |
| W2X//CCSD(T)-F12a/cc-pVTZ-F12 | -5.62 | 0.64 |
| W2X//CCSD(T)-F12a/cc-pVDZ-F12 | -5.66 | 0.68 |
| W2X//DF-CCSD(T)-F12b/VDZ(d) | -5.66 | 0.68 |
| W2X//DF-CCSD(T)-F12a/cc-pVDZ | -5.72 | 0.74 |
| W2X//DF-CCSD(T)-F12b/VDZ(NP) | -6.19 | 1.22 |

107 2.2 Electronic structure best estimates for R2-R9

108 **Geometrical optimization and frequency calculations.** Reliable optimized geometries and harmonic frequencies are
109 essential for obtaining quantitative 0 K activation enthalpies. For reaction R1, we verified that CCSD(T)-F12a/cc-pVDZ-F12
110 delivers results essentially identical to CCSD(T)-F12a/cc-pVTZ-F12, allowing us to employ the lower-cost cc-pVDZ-F12
111 basis for reaction R2. However, for larger CH₂OO + aldehyde systems, CCSD(T)-F12a/cc-pVDZ-F12 remains computationally
112 prohibitive. To overcome this limitation, we systematically benchmarked density-fitted F12 coupled-cluster methods (DF-
113 CCSD(T)-F12b) (Györfly and Werner, 2018) across a range of compact basis sets (Table 4). Remarkably, DF-CCSD(T)-
114 F12b/jun-cc-pVDZ (Parker et al., 2014) and DF-CCSD(T)-F12b/VDZ(d) exhibit exceptionally small mean unsigned
115 deviations of only 0.03 and 0.04 kcal mol⁻¹, respectively, relative to the Best Estimate for W2X reference (Table S2). This
116 identifies a new, computationally efficient F12 protocol capable of retaining sub-0.05 kcal mol⁻¹ accuracy for CH₂OO-

117 aldehyde reactions, representing a key methodological advance enabling routine treatment of larger Criegee intermediate–
118 carbonyl systems. Accordingly, we employed DF-CCSD(T)-F12b/jun-cc-pVDZ for R3–R5 and R7–R8, and DF-CCSD(T)-
119 F12b/VDZ(d) for R3–R6 to obtain geometries and vibrational frequencies with near-CBS accuracy at greatly reduced cost.

120 ***Single point energy calculations.*** To further reduce the cost of CCSDTQ/CBS-quality calculations, we developed a new
121 composite scheme, denoted BE1, which achieves near-GMMQ.L4 accuracy. The BE1 single-point energy is defined as

$$122 E_{\text{BE1}} = E_{\text{W2X}} + \Delta E_{(Q)-(T)} + \Delta E_{\text{SC1}} \quad (3)$$

123 where $\Delta E_{(Q)-(T)}$ is the CCSDT(Q) – CCSD(T) correction evaluated with the VDZ(NP) basis set for reactions R1–R8.

124 The term ΔE_{SC1} introduces a structure-specific correction and is given by

$$125 \Delta E_{\text{SC1}} = E_{\text{GMMQ.L4}}^{\text{TS1}} - E_{\text{W2X}}^{\text{TS1}} - [E_{\text{CCSDT(Q)/VDZ(NP)}}^{\text{TS1}} - E_{\text{CCSD(T)/VDZ(NP)}}^{\text{TS1}}] \quad (4)$$

126 This formulation anchors the composite energy to a single high-level reference transition state (TS1), ensuring the
127 transferability of the correction across the reaction series. The value of ΔE_{SC1} is 0.04 kcal/mol.

128 For comparison, we also employed our previously reported strategy, BE2 (Sun et al., 2024), which augments the W2X
129 energy with a constant post-CCSD(T) correction:

$$130 E_{\text{BE2}} = E_{\text{W2X}} + \Delta E_{\text{SC2}} \quad (5)$$

131 where ΔE_{SC2} is the GMMQ.L4 – W2X difference for TS1 (0.64 kcal mol⁻¹ in Table 4).

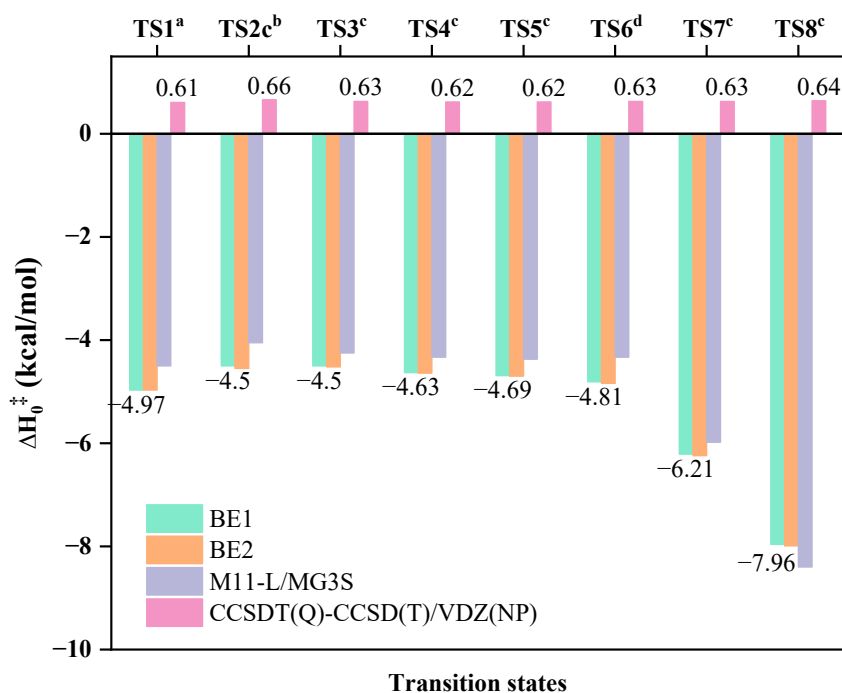
132 Both BE1 and BE2 offer computationally inexpensive routes to emulate CCSDTQ/CBS performance by incorporating
133 systematic, physically motivated corrections. In the present work, the BE1 protocol served as the high-level (HL) energy in
134 our dual-level kinetics strategy, with the underlying structures obtained from

- 135 • BE1//CCSD(T)-F12a/cc-pVDZ-F12 for R2,
- 136 • BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ for R3–R5 and R7–R8, and
- 137 • BE1//DF-CCSD(T)-F12b/VDZ(d) for R6.

138 This composite strategy enables sub-kcal mol⁻¹ accuracy at a fraction of the cost of full GMMQ.L4 or CCSDTQ/CBS
139 calculations.

140 **2.3. Electronic structure density functional methods**

141 To enable efficient direct kinetics calculations for the full aldehyde series, we systematically evaluated a range of density
 142 functional methods against the BE1 benchmark. Among all tested functionals, M11-L (Peverati and Truhlar, 2012)/MG3S
 143 (Lynch et al., 2003) exhibits the best performance, yielding a remarkably small mean unsigned deviation (MUD) of 0.32 kcal
 144 mol⁻¹ cross reactions R1–R8 (Figure 2). This accuracy—well within sub-kcal mol⁻¹ agreement with the BE1 high-level
 145 reference—identifies M11-L/MG3S as a reliable and computationally economical low-level (LL) method for the dual-level
 146 kinetics framework. Accordingly, M11-L/MG3S was used for all direct kinetics calculations involving CH₂OO + aldehyde
 147 reactions. Standard vibrational scaling factors were applied as listed in Table S3.



148 **Figure 2.** Best estimate for reaction R1-R8 at different level.
 149

150 ^aThe best estimate results by BE1//CCSD(T)-F12a/cc-pVTZ-F12 in the CH₂OO + HCHO reaction.

151 ^bThe best estimate results by BE1//CCSD(T)-F12a/cc-pVDZ-F12 in the CH₂OO + CH₃CHO reaction.

152 ^cThe best estimate results by BE1//DF-CCSD(T)-F12b/jun-cc-pVDZ in the CH₂OO + XCHO
 153 (X=C₂H₅/C₃H₇/C₄H₉/CH₂F/CHF₂) reaction.

154 ^dThe best estimate results by BE1//DF-CCSD(T)-F12b/VDZ(d) in the CH₂OO + C₅H₁₁CHO reaction.

155 Previous studies have suggested that standard scaling factors may be unsuitable for certain transition states, we explicitly

156 investigated the impact of anharmonicity. Using the method described by Long et al. (Long et al., 2023), we calculated specific
157 scaling factors by (See Tables S4 and S5). However, we found that anharmonicity corrections to the zero-point energy (ZPE)
158 were negligible. Consequently, standard scaling factors are employed throughout this work. Full methodological details are
159 provided in the Supporting Information.

160 **2.4. Kinetics Methods**

161 **High-pressure limited rate constants for R2-R6.** Dual-level strategy (Long et al., 2019; Sun et al., 2024; Long et al.,
162 2016) was employed, in which high-level (HL) conventional transition state theory (TST) provides the baseline rate constants,
163 whereas canonical variational transition state theory with small-curvature tunneling (CVT/SCT) at the low-level (LL) supplies
164 kinetic corrections. The high-pressure-limit rate constants were obtained according to eq 5:

$$165 \quad k = k_{\text{HL}}^{\text{TST}}(T) \kappa_{\text{LL}}(T) \Gamma_{\text{LL}}(T) F_{\text{fwd}}^{\text{MS-T,LL}}(T) \quad (5)$$

166 where $k_{\text{HL}}^{\text{TST}}$ is the rate constants calculated at HL. $\kappa_{\text{LL}}(T)$ and $\Gamma_{\text{LL}}(T)$ is tunneling and recrossing transmission coefficients
167 calculated at the LL level. $F_{\text{fwd}}^{\text{MS-T,LL}}(T)$ is referred to multi-structural anharmonic factor calculated by eqn (6) at the M11-
168 L/MG3S level

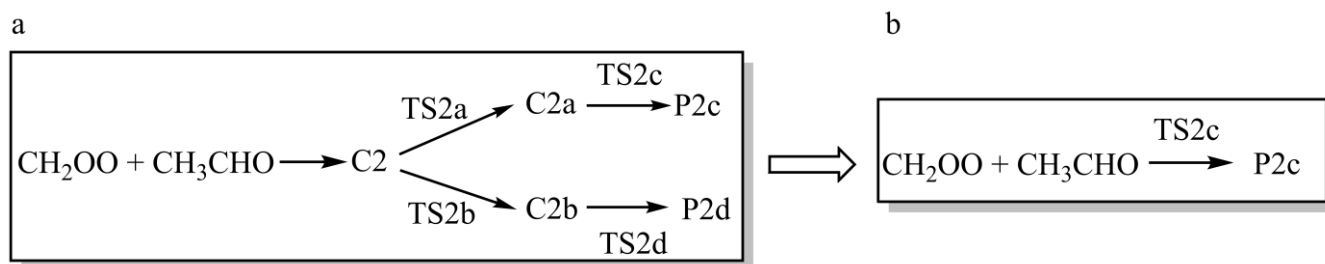
$$169 \quad F_{\text{fwd}}^{\text{MS-T,LL}} = \frac{F_{\text{TS}}^{\text{MS-T}}}{F_{\text{R}}^{\text{MS-T}}} \quad (6)$$

170 **High-pressure limited rate constants for R1 and R7-R9.** The rate constants of R1 and R7-R9 were calculated by
171 simultaneously considering both the loose transition state between reactants and the van der Waals complex, and the tight TS
172 between reactants and products. The rate constant for the loose TS (k_{loose}) was calculated using variable-reaction-coordinate
173 variational transition-state theory (VRC-VTST) (Georgievskii and Klippenstein, 2003; Zheng et al., 2008; Bao et al., 2016b)
174 with 500 configurations for Monte Carlo sampling. A single-faceted dividing surface was constructed with two pivot points,
175 following procedures validated in previous work (Long et al., 2021). One pivot point was placed along a vector at a distance
176 d from the center of mass (COM) of CH_2OO , oriented perpendicular to the CH_2OO plane, while the other was placed similarly
177 with respect to $\text{CH}_2\text{F}/\text{CHF}_2/\text{CF}_3\text{CHO}$. The pivot distance was set to $d=0.05$ Å. The reaction coordinate s was defined as the
178 separation between the two pivot points, ranging from 3.5 to 10 Å for R7, 3.9 to 10 Å for R8, 4.4 to 10 Å for R9 with increments

179 of 0.1 Å. The rate constant for the tight TS (k_{tight}) was calculated by using dual-level strategy presented above. The overall
180 rate constant was then obtained using the steady-state approximation (Garrett and Truhlar, 1982; Zhang et al., 2020; Long et
181 al., 2024) in equation (7).

$$182 \quad k = \frac{k_{\text{loose}}k_{\text{tight}}}{k_{\text{loose}}+k_{\text{tight}}} \quad (7)$$

183 **Pressure-dependent rate constant.** Master equation method with Rice–Ramsperger–Kassel–Marcus theory (ME/RRKM)
184 (Kenneth A. Holbrook, 1996; Fernández-Ramos et al., 2006; Georgievskii et al., 2013; Klippenstein, 2003) was used to
185 calculate pressure dependence of rate constants for the reactions of CH_2OO with HCHO and CH_3CHO . The calculation utilized
186 parameters from W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 for reaction R1 and W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ for
187 reaction R2. Both reactions were modeled with N_2 as the bath gas, employing Lennard-Jones parameters from Table S6 and
188 an average energy transfer parameter of $\langle\Delta E\rangle_{\text{down}} = 200 \text{ cm}^{-1}$. Within this framework, the pressure effect was approximated
189 as the quotient of the high-pressure limit and a pressure ratio. This ratio is defined as the value at $7.5 \times 10^3 \text{ Torr}$ relative to its
190 value at different pressures. We further inspection the simplification of reaction R2 in Scheme 2. The kinetic results for
191 Schemes 2a and 2b demonstrate remarkable robustness, with the simplification introducing no statistically significant
192 perturbations to the calculated rate constants.



195 **Scheme 2.** The reaction mechanism for the $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$ reaction.

196 2.5. Atmospheric modeling

197 We performed two atmospheric simulations included reaction R1 and R2 to investigate the significance of these reactions
198 by observing the change of concentration globally in GEOS-Chem. This included: (1) a “base” model using default setting (2)
a “update1” model adding a new sink of HCHO in the base model, (3) a “update2” model adding a new sink of CH_3CHO in

199 the base model. These models include the meteorological data observations assimilated from the NASA Modern-Era
200 Retrospective Analysis for Research and Applications (MERRA-2) (Gelaro et al., 2017) and Emissions data from the default
201 Harmonized Emission Component (HEMCO) (Lin et al., 2021). For anthropogenic emissions, we used the Community
202 Emissions Data System (CEDS) (Hoesly et al., 2018). For biogenic emissions, we used offline VOC emissions computed from
203 the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012). The simulation was carried out
204 with $2^\circ \times 2.5^\circ$ horizontal resolution at 47 vertical layers. The annual changes displayed are obtained from simulations that
205 employed meteorological data from February 1, 2018, to January 31, 2019, following a six-month model spin-up.

206 **2.6. Software.**

207 Density functional calculations were performed by using the Gaussian 16 (Frisch et al., 2016). The coupled cluster
208 calculations were performed by using the Molpro 2019 (Werner, 2019) and MRCC codes (Kállay et al., 2020). Multi-structural
209 anharmonic calculations were performed in MSTor codes (Zheng et al., 2012). Rate constants were calculated using the
210 Polyrate 2017-C (Zheng et al., 2017b), Gaussrate 2017-B codes (Zheng et al., 2017a), and KiSThIP 2021 (Canneaux et al.,
211 2014). The master equation calculations were performed by utilizing the TUMME program (Zhang et al., 2022). Atmospheric
212 modeling was performed by using GEOS-Chem 14.4.2 (Bey et al., 2001, (<http://www.geos-chem.org>, last access: 4 November
213 2025).

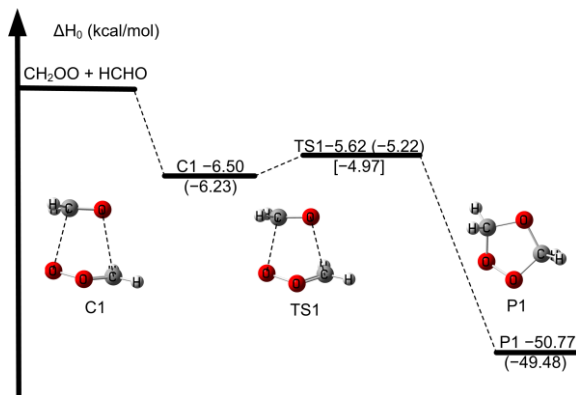
214 **3. RESULTS AND DISCUSSION**

215 The enthalpy of activation at 0 K (ΔH_0^\ddagger) is referred to the relative energies with zero-point energy between transition states
216 and reactants.

217 **3.1 The electronic structure of CH₂OO + HCHO**

218 The reaction mechanism examined here is consistent with that established in earlier studies (Luo et al., 2023; Long et al.,
219 2021; Jalan et al., 2013; Wang et al., 2022). The relative enthalpy profile for the CH₂OO + HCHO reaction is depicted in **Figure**
220 **3**, and the key data are summarized in Table 4. Notably, the activation enthalpy at 0 K obtained at the GMMQ.L4//CCSD(T)-

221 F12a/cc-pVTZ-F12 level (-4.97 kcal mol $^{-1}$) differs from that predicted by W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 (-5.21 kcal
222 mol $^{-1}$ in Table 4) and deviates even more substantially from the RCCSD(T)-F12a/VTZ-F12//B3LYP/MG3S value (-6.30 kcal
223 mol $^{-1}$) (Jalan et al., 2013). These differences demonstrate the strong sensitivity of ΔH_0^\ddagger to the underlying electronic-structure
224 treatment, thereby directly influencing predicted rate constants.



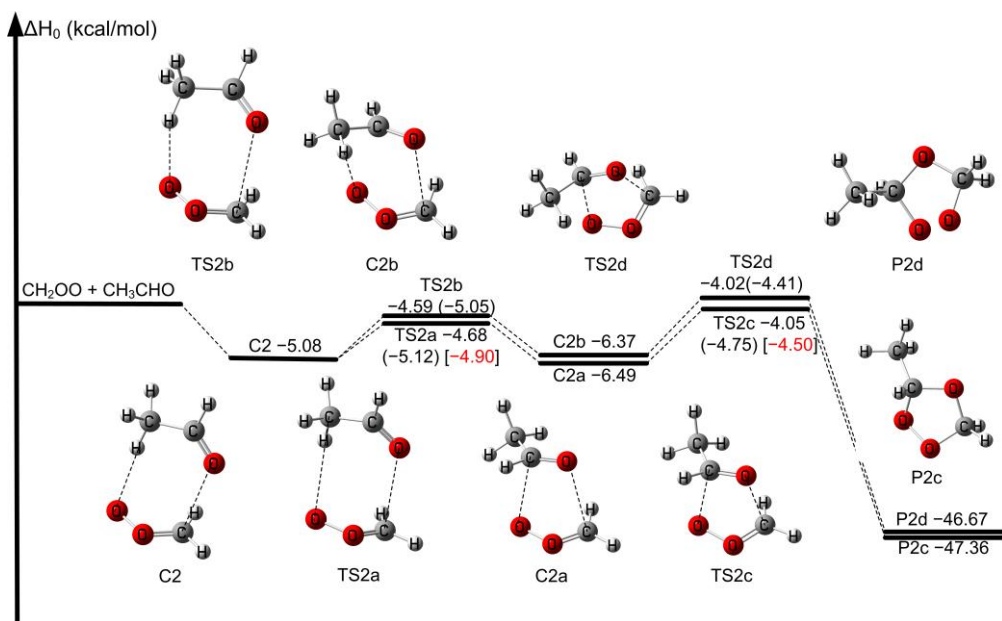
225
226 **Figure 3.** The relative enthalpies at 0 K for the reaction of CH₂OO + HCHO. Values are given for all species as calculated by
227 W2X//CCSD(T)-F12a/cc-pVTZ-F12, and in parentheses and bracket, values are given for the transition state TS1 as calculated
228 by W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 and GMMQ.L4//CCSD(T)-F12a/cc-pVTZ-F12.

229 Previous studies have shown that post-CCSD(T) correlation is essential for quantitative barriers in Criegee chemistry (Long
230 et al., 2021; Long et al., 2016; Xia et al., 2022). For TS1, the unsigned deviation between GMMQ.L4 and MW2-F12.L is 0.40
231 kcal mol $^{-1}$ —slightly different with the ~ 0.50 kcal mol $^{-1}$ benchmark established for post-CCSD(T) effects (Long et al., 2021)—
232 reaffirming the need for high-level correlation to achieve quantitative accuracy. We further find that the post-CCSD(T)
233 contribution through CCSDT(Q), quantified by the W3X-L – W2X difference, is 0.44 kcal mol $^{-1}$, in excellent agreement with
234 the 0.40 kcal mol $^{-1}$ value. This concordance highlights the robustness of W3X-L in capturing post-CCSD(T) contributions
235 (Table 4). The remaining 0.24 kcal mol $^{-1}$ discrepancy between GMMQ.L4 and W3X-L primarily reflects differences between
236 the MW2-F12.L and W2X components of TS1 (Tables S7 and S8). The 0.21 kcal mol $^{-1}$ deviation between MW2-F12.L and
237 W2X further illustrates that larger basis sets are required for fully quantitative predictions.

238 This present work provides a rigorously benchmarked assessment of ΔH_0^\ddagger for the CH₂OO + HCHO reaction, explicitly
239 quantifying post-CCSD(T) contributions and revealing their decisive role in achieving sub-kcal mol $^{-1}$ accuracy. The systematic
240 comparison among GMMQ.L4, MW2-F12.L, and W3X-L underscores the reliability of our calculated results.

241 3.2. The electronic structure of CH₂OO + CH₃CHO

242 We aim to demonstrate the feasibility of simplifying the reaction mechanism of larger aldehydes with CH₂OO in Scheme
 243 2. A partial reaction mechanism CH₂OO + CH₃CHO has been reported in our previous work (Wang et al., 2022). We first
 244 consider the seven-membered ring pre-reaction complex C2 formation in Figure 4, which is consistent with our previous results
 245 (Wang et al., 2022). However, due to two distinct orientations of the methyl group in CH₃CHO toward CH₂OO, there are two
 246 rotation transition states TS2a and TS2b connecting C2 to the five-membered ring complexes C2a and C2b, respectively.
 247 Therefore, the process is only the transformation of complex in the reaction processes. Then, C2a and C2b undergo the
 248 corresponding transition state TS2c and TS2d responsible for the formation of P2a and P2b. The mechanism was depicted in
 249 Scheme 2a. However, the enthalpies of activation at 0 K for TS2a and TS2b are lower than those of TS2c and TS2d by 0.64
 250 kcal/mol and 0.37 kcal/mol at W3X-L//CCSD(T)-F12a/cc-pVDZ-F12 in Figure 4, respectively. Therefore, TS2a and TS2b
 251 could be neglected from energetic point of view. We will also discuss it from the kinetics point of view.



252 **Figure 4.** The relative enthalpies at 0 K for the reaction of CH₂OO + CH₃CHO. Values are given for all species as calculated
 253 by M11-L/MG3S, and in parentheses and bracket, values are given for the transition states as calculated by W3X-L//CCSD(T)-
 254 F12a/cc-pVDZ-F12 and BE1//CCSD(T)-F12a/cc-pVDZ-F12.
 255

256 The five-membered ring complexes C2a and C2b can interconvert via TS2_{ISO} with C=O bond rotation, which lies 2.51

257 kcal mol⁻¹ above C2a at the M11-L/MG3S level (Figure S4), similar to the reaction between CH₂OO and FCHO (Xia et al.,
258 2024). For aldehydes with longer chains, the corresponding isomerization transition states of the five-membered ring
259 complexes (Figures S5–S6) exhibit similarly low barriers, indicating facile interconversion, which also verified from kinetics
260 perspective. Consequently, the complex mechanism can be effectively reduced to the straightforward reaction pathway b
261 depicted in Scheme 2. Accordingly, the mechanism for CH₂OO with larger aldehydes was simplified to consider only the
262 lowest-energy pathway corrected by torsional anharmonicity in kinetics calculations.

263 The ΔH_0^\ddagger for TS2c is -4.50 kcal mol⁻¹ at the BE1//CCSD(T)-F12a/cc-pVDZ-F12 level (See Table S9), which is 0.8 kcal
264 mol⁻¹ higher than the result reported by Jalan et al. at the RCCSD(T)-F12a/VTZ-F12//B3LYP/MG3S level and 0.19 kcal mol⁻¹
265 higher than that of Wang et al at the WMS//M11-L/MG3S level (Wang et al., 2022; Jalan et al., 2013). BE1 and BE2 for TS2c
266 agree well with each other in **Figure 2** and Table S9, not only demonstrating the reliability of the computational protocol, but
267 also capturing the essential physical origin underlying the quantitative description of ΔH_0^\ddagger . The M11-L/MG3S has been chosen
268 for direct dynamics calculations due to the MUD of 0.81 kcal mol⁻¹ in Table S9.

269 The validity of the DF-CCSD(T)-F12/jun-cc-pVDZ and DF-CCSD(T)-F12b/VDZ(d) methods was also confirmed for
270 reaction R2. As shown in Table S9, these methods yielded mean unsigned deviations (MUD) of 0.05 and 0.02 kcal mol⁻¹,
271 respectively, relative to the CCSD(T)-F12a/cc-pVDZ-F12 benchmark.

272 3.3. Electronic structure of CH₂OO + RCHO (R = C₂H₅/C₃H₇/C₄H₉/C₅H₁₁)

273 The complexity of reactions R3–R6 increases with reactant system size owing to the presence of multiple conformers of
274 both reactants and transition states (Table S10). Conformers for each reactant and transition state were obtained by rotating the
275 dihedral angles listed in Table S10. Specifically, two conformers were identified for C₂H₅CHO, four for C₃H₇CHO, twelve for
276 C₄H₉CHO, and thirty-five for C₅H₁₁CHO, arising from C–C bond rotations. In contrast, conformational diversity is even more
277 pronounced for the transition states, with three conformers for TS3, eighteen for TS4, twenty-four for TS5, and seventy-nine
278 for TS6, primarily due to internal C=O and C–C bond rotations.

279 As the carbon chain prolongs, the change in ΔH_0^\ddagger for R1-R6 is not obvious, but it presents a trend. We find a slight
280 decrease in ΔH_0^\ddagger with the elongation of carbon chain for R2-R6 with the exception of R1. The ΔH_0^\ddagger calculated by best

281 estimate are -4.50 , -4.50 , -4.63 , 4.69 , and -4.81 kcal mol⁻¹ for R2-R6 (See **Figure 2** and Table S11), which are about 3 kcal
282 mol⁻¹ below the reaction of the corresponding reactants with HO₂ (Gao et al., 2024; Long et al., 2022; Ding and Long, 2022).
283 Moreover, the influence of carbon chain length on enthalpy of activation for R2-R6 is analogue to the reaction of HO₂ and
284 aldehydes (Gao et al., 2024). Also, BE1 and BE2 for TS2c–TS6 (**Figure 2** and Table S11) exhibit excellent mutual consistency.
285 This behavior can be attributed to the nearly invariant $(\text{CCSDT(Q)} - \text{CCSD(T)})/\text{VDZ(NP)}$ term (~ 0.6 kcal mol⁻¹) among
286 these transition states, demonstrating that the post-CCSD(T) contributions are almost uniform across this reaction series. These
287 observations provide compelling evidence that both alkyl substitution and carbon-chain elongation negligibly modulate the
288 magnitude of post-CCSD(T) corrections, implying that such higher-order correlation effects are intrinsically insensitive to
289 substituent-induced electronic and conformational changes.

290 **3.4. Electronic structure of CH₂OO + RCHO (R = CH₂F/CHF₂/CF₃)**

291 The electronic structure information was depicted in **Figure 2** and Table S12. The activation enthalpies at 0 K decrease
292 significantly with the increasing number of fluorine substitutions in the methyl group of the aldehyde.

293 The ΔH_0^\ddagger for CH₂OO + CH₂FCHO (TS7) is -6.21 kcal mol⁻¹ by our best estimate, which is 1.31 kcal mol⁻¹ and 1.71
294 kcal mol⁻¹ lower than the reaction R1 and R2, respectively. Consequently, reaction R7 is expected to exhibit a significantly
295 larger rate constant compared to the CH₂OO + HCHO/CH₃CHO reactions. This reduction in ΔH_0^\ddagger indicates that fluorine
296 substitution enhances the reactivity of the aldehyde toward CH₂OO, which is similar to HO₂ + CF₃CHO (Long et al., 2022).
297 For the reaction of CH₂OO + CHF₂CHO (R8), the ΔH_0^\ddagger is -7.96 kcal mol⁻¹, which is 1.75 kcal mol⁻¹ lower than that of the
298 corresponding transition state, TS7. This value is close to that of CH₂OO + HCl (Foreman et al., 2016), which approaches the
299 bimolecular collision limit, suggesting that the reaction R8 through the tight transition state is not the rate-determining step.
300 Although fluorine substitution on the methyl group of the aldehyde leads to substantially enhanced reactivity toward CH₂OO,
301 the post-CCSD(T) contributions from the $(\text{CCSDT(Q)} - \text{CCSD(T)})/\text{VDZ(NP)}$ term (~ 0.6 kcal mol⁻¹) remain nearly identical
302 across the transition states as shown in **Figure 2**, revealing that the higher-order correlation effects are largely insensitive to
303 fluorination and establishing that the fluorination-driven reactivity enhancement originates primarily from lower-level
304 electronic effects than that of post-CCSD(T).

305 Given the demonstrated accuracy of the M11-L/MG3S method for reactions R7 and R8, this method was subsequently
306 applied to reaction R9, as depicted in Figure S3. Regarding $\text{CF}_3\text{CHO} + \text{CH}_2\text{OO}$ (R9), the ΔH_0^\ddagger further decreases to -9.74
307 kcal/mol at M11-L/MG3S level. However, this value is slightly higher than the activation enthalpies observed for the universal
308 mechanism of Criegee intermediates reacting with amides (Long et al., 2025), which are significantly submerged below the
309 reactants by approximately 9 to 11 kcal/mol. This shows that this tight transition state is not the rate-determining step for
310 reaction R9.

311 We further compare the calculated ΔH_0^\ddagger of the $\text{CH}_2\text{OO} + \text{RCHO}$ ($\text{R} = \text{CH}_2\text{F}, \text{CHF}_2, \text{CF}_3$) reactions with those of the
312 corresponding OH reactions. The ΔH_0^\ddagger for $\text{OH} + \text{CH}_2\text{FCHO}$ is -1.15 kcal mol $^{-1}$ at the CCSD(T)//M06-2X/aug-cc-pVTZ level,
313 which is 5.06 kcal mol $^{-1}$ higher than that of R7. We also find that the ΔH_0^\ddagger for R8 by our best estimate is 8.19 kcal mol $^{-1}$ lower
314 than that of $\text{OH} + \text{CHF}_2\text{CHO}$, calculated at the CCSD(T)/aug-cc-pVDZ//MP2(FC)/aug-cc-pVDZ level. The ΔH_0^\ddagger for R9
315 calculated by M11-L/MG3S is 11.94 kcal/mol lower than that of $\text{OH} + \text{CF}_3\text{CHO}$ at QCISD(T)/6-311G(d,p) level (Chandra et
316 al., 2001). The present findings reveal that the much lower ΔH_0^\ddagger for R7-R9 leads to a much faster rate constant, indicating
317 that oxidation by CH_2OO contributes significantly to the atmospheric loss of fluorinated aldehydes relative to the OH-initiated
318 pathway from energetic point of view.

319 **3.5. Kinetics**

320 **3.5.1 Pressure-dependent rate constants.**

321 The pressure dependence of the rate constants for reactions R1 and R2 was evaluated using the ME/RRKM framework,
322 with the results summarized in Tables S13–S15. As shown in Table S13, reaction R1 exhibits no appreciable pressure
323 dependence over the conditions examined, indicating that pressure effects can be safely neglected for this channel. This
324 conclusion is fully consistent with the findings reported by Luo et al (Luo et al., 2023). For example, the falloff factor calculated
325 for the $\text{CH}_2\text{OO} + \text{HCHO}$ reaction at 298 K and 0.0316 bar is 1.34 (Table S13). This factor, defined as the ratio of the rate
326 constant at 1000 bar to that at 0.0316 bar, indicates only a weak pressure dependence for this system. This result is in excellent
327 agreement with the findings reported by Luo et al. (Luo et al., 2023). We observed that at 295 K and 78 Torr, the pressure-

328 dependent rate constant was $2.71 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in Table S13, which is 7.74 times higher than the reported value
329 $((3.50 \pm 0.35) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ in Table 1 (Enders et al., 2024).

330 We assessed the validity of the simplified pathway by contrasting the full mechanism (Scheme 2a) with the model
331 (Scheme 2b) from a kinetic perspective as listed in Tables S13 and S14. The pressure-dependent rate constants obtained from
332 both models exhibit negligible deviations, thereby validating the simplified scheme as a computationally efficient strategy for
333 larger aldehydes. The calculated pressure-dependent rate constant for reaction R2 is $1.84 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 293 K
334 and 4 Torr in Table S14, in good agreement with the value of $(9.50 \pm 0.70) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Taatjes et al
335 (Taatjes et al., 2012). Our pressure-dependent rate constant at 298 K and 25 Torr corroborates the experimental value of $(1.20$
336 $\pm 0.20) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Elsamra et al ($1.65 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in Table S14) (Elsamra et al.,
337 2016). We found that the fall-off factor is only 1.36 (Table S14) for the reaction R2 at 298 K and 4 Torr, which also shown that
338 the rate constant of reaction R2 is negligibly pressure-dependent, which confirms the experimental results qualitatively (Enders
339 et al., 2024; Stone et al., 2014; Berndt et al., 2015; Jiang et al., 2024). In addition, there is experimental evidence that the
340 pressure effect is also insignificant for propionaldehyde and butyraldehyde (Liu et al., 2020; Debnath and Rajakumar, 2024).

341 3.5.2 High pressure limit rate constants

342 High-pressure limit rate constants for all reactions are summarized in Table 5, with additional details provided in Tables
343 S16–S24. The rate constants in the temperature range of 190–350 K were fitted using the four-parameter expression (Zheng
344 and Truhlar, 2012; Bao et al., 2016a):

$$345 k_{\infty} = A \left(\frac{T+T_0}{300} \right)^n \exp \left[-\frac{E(T+T_0)}{R(T^2+T_0^2)} \right] \quad (7)$$

346 Where R is the gas constant, T is temperature in K, the fitting parameters were listed in Table S25. The temperature dependence
347 of the Arrhenius activation energies was further calculated using the following expression:

$$348 E_a = -R \frac{d \ln k_{\infty}}{d(1/T)} \quad (8)$$

349
350 **Table 5.** The high-pressure limiting rate constants ($\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of the $\text{CH}_2\text{OO} + \text{RCHO}$ (R =
351 H/ CH_3 / C_2H_5 / C_3H_7 / C_4H_9 / C_5H_{12} / CH_2F / CHF_2 / CF_3) reaction

| T/K | k_1 | k_2 | k_3 | k_4 | k_5 | k_6 | k_7 | k_8 | k_9 |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 200 | 426 | 96 | 105 | 115 | 106 | 214 | 430 | 451 | 740 |
| 220 | 297 | 32.7 | 36.1 | 40.8 | 36 | 71.9 | 248 | 416 | 688 |
| 240 | 171 | 13.6 | 15 | 17.5 | 14.8 | 29.5 | 115 | 381 | 652 |
| 260 | 90.4 | 65.4 | 7.27 | 8.72 | 6.75 | 13.1 | 51.1 | 328 | 626 |
| 280 | 48.0 | 3.55 | 3.93 | 4.86 | 3.64 | 7.09 | 24 | 252 | 607 |
| 298 | 28.3 | 2.27 | 2.45 | 3.10 | 2.28 | 4.46 | 13.1 | 182 | 594 |
| 300 | 26.8 | 2.11 | 2.34 | 2.97 | 2.22 | 4.41 | 12.3 | 174 | 593 |
| 320 | 15.9 | 1.35 | 1.49 | 1.95 | 1.37 | 2.67 | 6.90 | 110 | 583 |
| 340 | 10.0 | 9.22 | 1.01 | 1.35 | 0.93 | 1.80 | 4.17 | 67.4 | 576 |

352 **The reaction of $\text{CH}_2\text{OO} + \text{HCHO}$.** As summarized in Table 1 and [Figure 1](#), a long-standing order-of-magnitude
353 discrepancy exists between previously reported experimental and theoretical rate constants for reaction R1. At 296 K, the rate
354 constant obtained in this work is $3.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in Table 1, which is 7.31 times larger than the experimental
355 value reported by Luo et al (Luo et al., 2023), but 1.83 and 2.17 times smaller than the theoretical predictions of Zhang et al.
356 (Zhang et al., 2023) and Long et al. (Long et al., 2021), respectively. We therefore consider two plausible explanations: The
357 experimental determination of CH_2OO kinetics may introduce systematic uncertainties. Alternatively, subtle dynamic effects
358 beyond conventional transition state theory (e.g., non-statistical dynamics or complex-forming behavior) may play a role and
359 require further investigation. Although the present value does not fully reconcile the experimental and theoretical results, it
360 substantially narrows the gap between the two, providing a quantitatively improved estimate for this key reaction.

361 Notably, the derived rate constant for R1 is approximately 8 times larger than that for the corresponding OH-initiated
362 reaction and more than two orders of magnitude larger than that for the HO_2 -initiated pathway (Long et al., 2022; Sivakumaran
363 et al., 2003), highlighting the unexpectedly high reactivity of CH_2OO in this system. These findings underscore the need for
364 further high-precision experimental measurements and establish the present computational protocol as a robust framework for
365 resolving persistent discrepancies in atmospheric reaction kinetics.

366 **The reaction of $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$.** To date, no theoretical kinetic studies have been reported for the $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$
367 reaction in Table 2. The earliest experimental determination yielded a rate constant of $(9.50 \pm 0.25) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
368 at 293 K and 4 Torr, as measured by Taatjes et al. (Taatjes et al., 2012), which is a factor of 2.9 smaller than the present
369 theoretical prediction in Table 2. At 298 K, the calculated rate constant for reaction R2 is $2.50 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in

370 Table 2, in excellent agreement with the experimental values reported by Elsamra et al. (Elsamra et al., 2016) and Jiang et al.
371 (Jiang et al., 2024) In addition, the value measured by Berndt et al. (Berndt et al., 2015) at 297 K, $(1.7 \pm 0.50) \times 10^{-12} \text{ cm}^3$
372 $\text{molecule}^{-1} \text{ s}^{-1}$, is fully consistent with our calculated result of $2.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in Table 2. Overall, the rate
373 constants obtained in this work are in good agreement with the available experimental data (Elsamra et al., 2016; Stone et al.,
374 2014; Berndt et al., 2015; Jiang et al., 2024; Cornwell et al., 2023), providing the first reliable theoretical benchmark for the
375 kinetics of the $\text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$ reaction. Notably, the rate constant for R2 is approximately 5.6 times smaller than that for
376 the corresponding OH-initiated reaction, yet nearly two orders of magnitude larger than that for the HO_2 -initiated pathway,
377 highlighting the distinct and non-negligible role of CH_2OO in aldehyde oxidation chemistry (Long et al., 2022; Zhu et al.,
378 2008). The five-membered ring species C2a and C2b readily interconvert, as the rate constant for the isomerization process is
379 approximately two orders of magnitude larger than that of the addition reaction (Table S26).

380 ***The reaction of $\text{CH}_2\text{OO} + \text{RCHO}$ ($\text{R}=\text{C}_2\text{H}_5/\text{C}_3\text{H}_7/\text{C}_4\text{H}_9/\text{C}_5\text{H}_{11}$).*** Rate constants for the reactions of CH_2OO with
381 $\text{C}_2\text{H}_5\text{CHO}$ have been reported previously from both experimental and theoretical studies (See Table 3) (Enders et al., 2024;
382 Kaipara and Rajakumar, 2018; Liu et al., 2020), whereas the reaction with $\text{C}_3\text{H}_7\text{CHO}$ has been examined only experimentally.
383 At 298 K, the calculated rate constant for $\text{CH}_2\text{OO} + \text{C}_2\text{H}_5\text{CHO}$ is $3.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table 3), in excellent
384 agreement with the experimental value reported by Liu et al (Liu et al., 2020).

385 For $\text{CH}_2\text{OO} + \text{C}_3\text{H}_7\text{CHO}$, the calculated rate constant of $3.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table 3) closely reproduces the
386 experimental value of $(2.63 \pm 0.14) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Debnath and Rajakumar, 2024), further validating the reliability
387 of the present computational protocol. To the best of our knowledge, no prior experimental or theoretical studies have reported
388 rate constants for the reactions of CH_2OO with pentanal or hexanal. Our calculations indicate that the rate constant for CH_2OO
389 + $\text{C}_4\text{H}_9\text{CHO}$ is comparable to that for CH_3CHO , whereas the rate constant for $\text{CH}_2\text{OO} + \text{C}_5\text{H}_{11}\text{CHO}$ is approximately twice as
390 large, yet remains within the same order of magnitude (Table 5). These results demonstrate that increasing alkyl chain length
391 exerts only a minor influence on the reaction kinetics of CH_2OO with aldehydes, revealing a weak and nonmonotonic size
392 dependence across the C_1 – C_5 series. This behavior is fully consistent with the computed activation enthalpies (See **Figure 2**)
393 and establishes a transferable structure–reactivity relationship for CH_2OO reactions with larger aldehydes. Overall, aside from
394 formaldehyde, the rate constants for CH_2OO reactions with alkyl-substituted aldehydes vary only modestly, underscoring the

395 limited role of substituent size in governing CH₂OO reactivity.

396 **The reaction of CH₂OO + RCHO (R=CH₂F/CHF₂/CHF₃).** A striking fluorination-induced reactivity enhancement
397 emerges upon substitution of hydrogen atoms on the methyl group. Introduction of fluorine leads to a pronounced increase in
398 the rate constants for CH₂OO + CH₃CHO reactions, revealing an unexpected structure–reactivity trend. At 298 K, the rate
399 constant for reaction R7 is $1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Table 5), which is about 6 times larger than that of R2 and about 5
400 times larger than the corresponding OH + CH₂FCHO reaction (Lily et al., 2021).

401 Even more dramatic behavior is observed for reactions R8 and R9. For R8, the calculated rate constants approach the
402 collision limit, decreasing slightly from $4.51 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K to $6.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 340 K
403 in Table 5, indicating of a weak negative temperature dependence characteristic of barrierless processes. Notably, at 298 K the
404 reaction of CHF₂CHO with CH₂OO is more than two orders of magnitude faster than its reactions with OH [$(1.8 \pm 0.4) \times 10^{-12}$
405 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] (Sellevåg et al., 2005), underscoring the unusually high reactivity of CH₂OO toward fluorinated aldehydes.

406 The most pronounced effect is found for R9, for which the rate constant ranges from $7.40 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at
407 200 K to $5.76 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 340 K in Table 5, fully approaching the collision limit and exceeding the
408 corresponding OH-initiated reaction rates by orders of magnitude. These results demonstrate that fluorination fundamentally
409 alters the reaction landscape of CH₂OO with aldehydes, transforming otherwise moderately fast bimolecular reactions into
410 near-collision-controlled processes.

411 3.6. Atmospheric Implications

412 The reaction of aldehydes with OH have been investigated extensively experimentally and theoretically. Here, we
413 considered the competition for aldehydes relative to CH₂OO and OH. the ratio of reaction rate was calculated by eqn (9):

$$414 \quad v_i = \frac{k_i[\text{CH}_2\text{OO}]}{k_{\text{OH},i}[\text{OH}]} \quad (9)$$

415 where the k_i is the rate constants for the reaction R2-R9, $k_{\text{OH},i}$ is the rate constant of OH + RCHO (R = CH₃, C₂H₅, C₃H₇, C₄H₉,
416 C₃H₁₁, CH₂F, CHF₂, CF₃), and i is referred to is equal to 2-9. The concentrations of CH₂OO and OH exhibit pronounced
417 geographical and spatial distributions. The concentration of OH is varied from 10^4 - 10^6 molecules cm^{-3} (Khan et al., 2018; Ren
418 et al., 2003; Stone et al., 2012), and the estimated concentration for CH₂OO is range from 10^4 to 10^5 molecules cm^{-3} (peaking

419 at 6×10^5 molecules cm^{-3}) (Lelieveld et al., 2016; Novelli et al., 2017) In contrast, the base-version model simulations yield
 420 CH_2OO concentrations approximately one order of magnitude lower than the estimated value. This discrepancy likely
 421 originates from (i) the adoption of relatively fast rate constants for CH_2OO loss via reactions with H_2O and $(\text{H}_2\text{O})_2$, and (ii) an
 422 incomplete representation of CH_2OO sources in the model framework. Consequently, the use of model-derived concentrations
 423 probably leads to an underestimation of the contribution of CH_2OO to aldehyde removal.

424 Our results demonstrate that for aliphatic aldehydes, reactions with CH_2OO constitute a negligible sink compared with OH
 425 oxidation, owing to both modest rate constants and low ambient CH_2OO concentration (See Tables S27–S29). Although
 426 fluorine substitution generally enhances reactivity, the increase in the rate constant for CH_2FCHO remains insufficient to
 427 meaningfully compete with the OH pathway. Effective competition is predicted only under highly specific conditions—namely,
 428 nighttime at ~ 10 km altitude over the Malaysian region (Table 6). In stark contrast, the reactions of highly fluorinated aldehydes
 429 with CH_2OO proceed at near-collision-limit rates. As a result, CH_2OO constitutes a major atmospheric sink for CHF_2CHO and
 430 CF_3CHO . As summarized in Table 6, CH_2OO competes effectively with OH for CHF_2CHO at night near the surface over
 431 Russia and the Arctic, influences its removal at 5 km over Russia and Indonesia, and contributes significantly at 10 km over
 432 Indonesia. Notably, because the reaction of CF_3CHO with OH is intrinsically slow, CH_2OO dominates its atmospheric removal
 433 over Indonesia at all altitudes considered, while in the Russian region its influence is confined to 0 and 5 km.

434 **Table 6.** rate concentration ratios CH_2OO to OH and the rate ratio at different heights from different region

| Height | T/K | P/mBar | $[\text{CH}_2\text{OO}]/[\text{OH}]^a$ | v_8^b | v_9^c |
|--------------|-------|--------|--|-----------------------|-----------------------|
| Gansu, China | | | | | |
| 1 | 290.2 | 1013 | 2.48×10^{-4} | 2.89×10^{-2} | 2.29×10^{-1} |
| 5 | 250.5 | 495.9 | 3.09×10^{-4} | 6.25×10^{-2} | 3.03×10^{-1} |
| 10 | 215.6 | 242.8 | 3.51×10^{-5} | 8.14×10^{-3} | 3.77×10^{-2} |
| Russia | | | | | |
| 1 | 290.2 | 1013 | 1.52×10^{-2} | 1.77 | 14 |
| 5 | 250.5 | 495.9 | 6.39×10^{-3} | 1.29 | 6.26 |
| 10 | 215.6 | 242.8 | 3.23×10^{-5} | 7.48×10^{-3} | 3.47×10^{-2} |
| Arctic | | | | | |
| 1 | 290.2 | 1013 | 1.15×10^{-2} | 1.33 | 10.6 |
| 5 | 250.5 | 495.9 | 5.16×10^{-4} | 1.04×10^{-1} | 5.05×10^{-1} |
| 10 | 215.6 | 242.8 | 1.91×10^{-6} | 4.43×10^{-4} | 2.05×10^{-3} |

| Indonesia | | | | | |
|-----------|-------|-------|-----------------------|-----------------------|------|
| 1 | 290.2 | 1013 | 3.16×10^{-3} | 3.67×10^{-1} | 2.91 |
| 5 | 250.5 | 495.9 | 5.85×10^{-3} | 1.18 | 5.74 |
| 10 | 215.6 | 242.8 | 2.53×10^{-2} | 5.87 | 27.2 |

435 ^aThe concentration ratio between CH₂OO and OH from GEOS-Chem.

436 ^bThe rate ratio between CH₂OO + CHF₂CHO and CHF₂CHO + OH.

437 ^cThe rate ratio between CH₂OO + CF₃CHO and CF₃CHO + OH.

438 Overall, these findings reveal a qualitative shift in aldehyde oxidation pathways upon heavy fluorination, identifying
 439 CH₂OO as a previously underappreciated but potentially dominant oxidant for highly fluorinated aldehydes under specific
 440 atmospheric regimes—an effect with important implications for the atmospheric lifetimes of emerging fluorinated oxygenated
 441 VOCs.

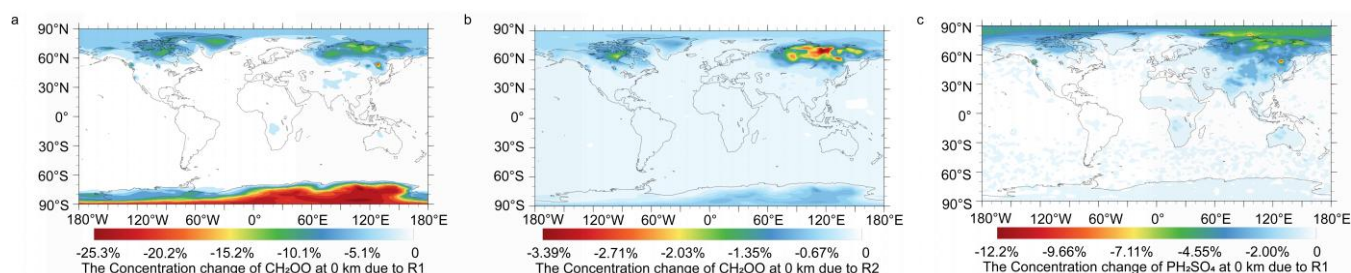
442 3.7. Atmospheric modelling

443 Model simulations were further performed to assess the atmospheric significance of nighttime reactions between CH₂OO
 444 and aldehydes. The Criegee intermediate (CI) chemistry implemented in the base model has been described in our previous
 445 work (Long et al., 2024). In this study, two targeted updates were introduced to isolate and quantify the impacts of newly
 446 identified CI–aldehyde reaction pathways. The first update incorporates the CH₂OO + HCHO reaction into the base mechanism,
 447 reflecting an improved understanding of CI removal under aldehyde-rich nighttime conditions. The second update further
 448 expands the CI sink by including the reaction between CH₂OO and CH₃CHO, thereby providing a more comprehensive
 449 representation of acetaldehyde-driven CI loss. The aldehyde chemistry employed in the model is summarized in Table S30.
 450 We do not consider the impact of CH₂OO on fluorinated aldehyde sinks by using GEOS-Chem, as fluorinated aldehydes are
 451 not involved in the current default GEOS-Chem version.

452 The simulated aldehyde concentrations exhibit pronounced spatial and vertical heterogeneity. Surface-level HCHO
 453 concentrations reach up to 1.46×10^{11} molecules cm⁻³, while CH₃CHO attains maxima of 8.06×10^{10} molecules cm⁻³, with
 454 the highest abundances over Malaysia and Indonesia. These values are consistent with field observations, which report peak
 455 HCHO concentrations of up to 3.63×10^{11} molecules cm⁻³ (Hu et al., 2025), lending confidence to the model performance.
 456 The simulated global mean surface concentration of CH₃CHO (5.89×10^9 molecules cm⁻³, corresponding to ~200 ppt) is in

457 reasonable agreement with observational constraints and remains lower than values reported by Komazaki et al (Komazaki et
458 al., 1999; Tereszchuk and Bernath, 2011).

459 The contribution of HCHO to the reduction of CH₂OO has been assessed in our prior work and is once again validated
460 by model simulations (Long et al., 2021). Figure 5 shows the relative changes in annual mean surface-layer CH₂OO
461 concentrations resulting from the inclusion of the CH₂OO + HCHO (R1) and CH₂OO + CH₃CHO (R2) reactions. Incorporation
462 of the updated rate constant for R1 leads to a pronounced reduction in CH₂OO, with a maximum decrease of 25.3% over the
463 Antarctic region (Figure 5), highlighting the previously unrecognized importance of HCHO as a nighttime CI sink. In contrast,
464 R2 produces a more modest effect, with a maximum CH₂OO reduction of 3.39% over Russia in Figure 5.



465 **Figure 5.** Changes in global CH₂OO concentrations due to reaction R1 and R2 (a) reaction R1, (b) reaction R2, and (c) changes
466 in global sulfate concentrations due to reaction R1.
467

468 Despite the substantial impact on CI abundances, the direct effects on aldehyde concentrations remain small. As shown in
469 Figure S8, surface acetaldehyde decreases by only 0.12% in the Arctic. However, the influence on secondary oxygenated
470 products is more pronounced. As illustrated in Figure S9, inclusion of R1 enhances formic acid concentrations by up to 5.44%
471 over Canada and Russia, while acetic acid increases by as much as 0.69% in the Arctic. These results demonstrate that CI-
472 aldehyde reactions, while exerting limited feedback on aldehydes themselves, can make significant contribution to the sinks
473 of CH₂OO and the formation of atmospheric acids.

474 The potential implications of reaction R1 for regional air quality were also assessed, particularly regarding the mitigation of
475 gas-phase sulfate formation. We found that the concentration of gas-phase sulfate can reach 10⁸ molecules cm⁻³ in Mexico
476 region in Figure S10. The inclusion of this reaction pathway effectively lowers the concentration of CH₂OO, thereby
477 diminishing its capacity to oxidize SO₂ into sulfuric acid precursors. This depletion of oxidative capacity leads to a marked
478 decrease in gas-phase sulfate concentration. The effect is geographical, with the reduction in gas-phase sulfate concentrations

479 estimated to be 12.2% in Canada and 6.01% in Russia during the nighttime in Figure 5c. While the relative changes might
480 initially imply a substantial regional sink for atmospheric sulfate aerosols, a detailed comparison of Figures 5c and S10 reveals
481 that the largest percentage changes in gas-phase sulfate predominantly occur in regions with low baseline concentrations.
482 Specifically, although peak concentrations over Canada and Russia reach $\sim 10^7$ molecules cm^{-3} , their regional averages remain
483 on the order of 10^5 molecules cm^{-3} . In contrast, regions with much higher absolute concentrations (e.g., $\sim 1 \times 10^8$ molecules
484 cm^{-3} over Mexico) exhibit only minimal relative changes. This indicates that modest absolute variations can produce large
485 percentage changes under low-background conditions, whereas comparable or even larger absolute changes appear
486 insignificant in high-concentration environments. Consequently, this reaction has a negligible impact on the global atmospheric
487 sulfate burden.

488 4. CONCLUSIONS

489 The present work establishes a transferable and systematically improvable theoretical framework for predicting quantitative
490 atmospheric reaction kinetics across molecular complexity, using the reactions of CH_2OO with a series of aldehydes as a
491 definitive test case. By explicitly approaching the full configuration interaction (CI) limit for the benchmark $\text{CH}_2\text{OO} + \text{HCHO}$
492 system, we delineate the accuracy requirements necessary for reliable kinetic predictions and provide a rigorous reference
493 against which lower-cost methods can be assessed. Energetic and kinetic analyses validate a simplified reaction mechanism,
494 attributed to the facile interconversion between complexes and the energetic preference for rotational transition states over
495 addition pathways.

496 Guided by the detailed electronic-structure insights obtained for $\text{CH}_2\text{OO} + \text{HCHO}$, we develop a computational protocol
497 that integrates optimized geometries, vibrational frequencies, and high-level single-point energies, enabling accurate kinetics
498 for larger systems at feasible computational cost. We find that DF-CCSD(T)-F12b/VDZ(d) and DF-CCSD(T)-F12b/jun-cc-
499 pVDZ can be used to reliably describe the optimized geometries and calculated frequencies. two generalizable strategies (BE1
500 and BE2) have been used to recover the CCSDTQ/CBS level single point energies, which provide new insight into how to
501 obtain the quantitative enthalpy of activation.

502 In kinetics calculations, for reactions with appreciable barriers (R2–R6), this dual-level strategy yields robust rate
503 constants, whereas for reactions characterized by exceptionally low or submerged barriers (R1 and R7–R9), the explicit
504 application of VRC-VTST proves essential for capturing the correct dynamical behavior. This demonstrates a practical pathway
505 for extending benchmark-level kinetics from small to chemically diverse, larger molecules.

506 The resulting kinetic trends reveal that alkyl-chain elongation exerts only a minor influence on reactivity, whereas fluorine
507 substitution dramatically enhances reaction rates, driving the $\text{CH}_2\text{OO} + \text{CHF}_2\text{CHO}$ and $\text{CH}_2\text{OO} + \text{CF}_3\text{CHO}$ reactions toward
508 the collision limit. All reactions exhibit negligible pressure dependence, underscoring their relevance under atmospheric
509 conditions. These high-precision rate constants provide a mechanistically grounded explanation for the increasingly important
510 role of Criegee intermediates in the oxidation of fluorinated aldehydes. We find that fluorine substitution on aldehydes
511 dramatically enhances their reactivity toward CH_2OO ; however, the post-CCSD(T) contributions remain almost equal across
512 the reaction series. This behavior indicates that fluorination-driven rate acceleration is governed primarily by lower-level
513 electronic effects rather than by higher-order electron correlation than CCSD(T). This observation also provides a fundamental
514 basis for the development of high-accuracy semiempirical correction schemes.

515 Beyond molecular-scale kinetics, global and regional modeling demonstrates that while reactions of CH_2OO with HCHO
516 and CH_3CHO contribute negligibly to aldehyde removal, HCHO constitutes a major global sink for Criegee intermediates,
517 accounting for a 25.3% reduction in the global CH_2OO burden during the night. In contrast, fluorination fundamentally alters
518 atmospheric fate: for CH_2FCHO , CH_2OO reactions become regionally significant (e.g., near 10 km altitude over Malaysia),
519 and for more heavily fluorinated aldehydes such as CHF_2CHO , CH_2OO overwhelmingly dominates over OH-initiated loss
520 pathways. The associated enhancement in acid formation, although modest, further highlights the chemical implications of
521 these processes. The inclusion of reaction R1 results in a reduction of gas-phase sulfate levels by 12.2% over Canada and 6.01%
522 over Russia. These present findings deliver a generalizable, benchmark-anchored strategy for quantitative kinetic prediction,
523 bridges electronic-structure theory with atmospheric modeling, and reveals how fluorination reshapes the atmospheric
524 relevance of Criegee intermediates—insights that are critical for atmospheric chemical mechanisms.

525

526

527 **Supplement.** The following information is provided in the Supplement: Details of reaction R9, enthalpies of binding and
528 activation and barrier height; vibrational frequency scale factors; Lennard-Jone parameters; Rate constants and rate constant
529 fits; Rate ratio; Absolute energies and the Cartesian coordinates and absolute energies; relative enthalpies for reaction of R3-
530 R9; Enthalpy profile for the conversion of pre-reaction complex; Changes in global CH₃CHO, HCOOH, and CH₃COOH
531 concentrations.

532
533 **Data and code availability.** Electronic structure calculations were performed using commercially available software
534 (Gaussian 16, Revision A.03 and Molpro 2019). Access to the software is subject to licensing terms. The MRCC and
535 MStor codes can be accessed at <https://www.mrcc.hu> and <https://comp.chem.umn.edu/mstor>, respectively. Polyrate 2017-C
536 and Gaussrate 2017-B are available at <https://comp.chem.umn.edu/polyrate> and <https://comp.chem.umn.edu/gaussrate>.
537 KiSThLP 2021 is accessible at <http://kisthelp.univ-reims.fr>, and the TUMME program can be found at
538 <https://comp.chem.umn.edu/tumme>. The GEOS-Chem 14.4.2 is available at <http://www.geos-chem.org>. Optimized
539 geometries, and calculated energies are available in Supplement. Other data are available from the corresponding
540 author upon reasonable request.

541
542 **Author contributions.** CX carried out the calculations, analysed and interpretation of data, and wrote the manuscript
543 draft. BL designed the project, analysed and interpretation of data, and reviewed and edited the manuscript.

544
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546
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