Manuscript ID: egusphere-2026-119
Title: "Reactions of Carbonyl Oxide with Aldehydes: Accurate Electronic Structure Methods, Kinetic Insights, and Atmospheric Implications"
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Responses in blue.

RC2

The order-of-magnitude difference between experimental and theoretical rate constants for the CH_2OO + HCHO reaction is a big question whose resolution is highly significant. The theoretical rate constants presented in this manuscript clearly agree better with experiment than previous theoretical predictions (Figure 4), but it would be worthwhile to suggest at least one reason for the remaining discrepancy.
Author response: Thanks for your comments.

The authors make solid arguments for why CH_2OO ought to be include alongside OH and HO_2 as significant aldehyde oxidants in the atmosphere. The prediction that fluorinated aldehydes react with CH_2OO at near the collision limit is highly significant.
The new electronic structure approaches that allow for the achievement of sub-kcal/mol accuracy for systems with eight non-hydrogen atoms is an impressive methodological advance.
The authors report the useful result that post-CCSD(T) corrections (*i.e.* very high levels of electron correlation) are not necessary for accurate reaction barriers as fluoro or longer alkyl substituents are added to aldehydes.
Author response: Thanks for your comments.

Scientific quality
1). On p. 4, the authors mention the common use of structure-reactivity relationships such as those proposed by Jenkin et al. It would be good to circle back to them at some point in the manuscript, as the reliability of these estimation methods is an important issue for the atmospheric chemistry community.
Author response: Thanks for your comments. We agree that while the structure-reactivity relationships (SARs) developed by Jenkin et al. are widely used for their efficiency in large-scale models. We will rephase the sentence in the revised version "To address these gaps, atmospheric models have effectively utilized rate constants derived from empirical structure–reactivity relationships (SRRs)—such as those proposed by Jenkin et al. (Jenkin et al., 2018)—which provide a practical and robust framework for large-scale modeling. Given the inherent complexity of computing atmospheric kinetics, these empirical methods remain a primary tool for estimation." in page 4.

2). Related to ways that the presentation quality can be improved (see below), the authors should briefly explain why their methodology is better than the methods of Chan and Radom. Specifically, the authors should briefly explain why W3X-L is not sufficient for describing post-CCSD(T) effects (p. 7). Also, why is the MW2-F12.L energy corrected stepwise by T-(T) and (Q)-T terms (equation 1), while the W2X energy can be corrected by one term from the (T) level to the (Q) level (equation 3)?

Author response: Thanks for your comments. The discrepancy of 0.24 kcal/mol highlights that for the CH_2OO + HCHO reaction, the basis set requirements for the CCSD(T) base energy and subsequent high-order corrections are critical. GMMQ.L4 addresses this by leveraging the MW2-F12.L scheme to provide a more robust CCSD(T) foundation than the W2X component of W3X-L due to larger basis set listed in Table S7 and S8. The stepwise framework enables the T-(T) and (Q)-T terms to utilize larger basis sets to approach the CBS limit, whereas the Q-(Q) are handled with a meticulously selected smaller basis set to maintain computational feasibility. Additionally, our inclusion of full CCSDTQ rather than the perturbative CCSDT(Q) ensures that the post-CCSD(T) effects are described with higher theoretical fidelity. We will rephase the description in the revised version "We further compared GMMQ.L4 with the W3X-L composite method (Chan and Radom, 2015) for reaction R1. Although both protocols include identical post-CCSD(T) contributions, GMMQ.L4 employs the MW2-F12.L component, whereas W3X-L is based on W2X. Detailed comparisons are provided in Tables S1, S7, and S8. The observed deviation of 0.24 kcal mol^{-1} indicates that W3X-L does not achieve quantitatively reliable barrier heights for this system. Our analysis shows that this discrepancy primarily originates from the difference between MW2-F12.L and W2X. Specifically, MW2-F12.L includes HF energies, ΔCCSD and Δ(T) correlation contributions, core–valence (Δ(C+V)) corrections, and scalar relativistic (Δ(C+R)) effects, all evaluated with larger basis sets. In contrast, W2X comprises analogous HF, ΔCCSD, Δ(T), and Δ(C+R) terms, but these are computed using smaller basis sets. The calculated results the difference of 0.24 kcal mol^{-1} comes from the Δ(C+V) and Δ(C+R) terms, which differ by 0.19 kcal/mol and 0.12 kcal/mol, respectively." in page 7.

3). On p. 15, there is an assertion that the interconversion TS between C2a and C2b has a low barrier that leads to facile interconversion. However, the M11L $TS2_{ISO}$ 0 K enthalpy is -3.98 kcal/mol, which is essentially identical to the enthalpy of TS2d and higher than the enthalpy of TS2c. Thus, it does not seem obviously valid to assume rapid interconversion of the two five-membered ring complexes.

Author response: Thanks for your comments. To further validate our assertion of "facile interconversion", we calculated the rate constants for these processes. Our kinetic analysis reveals that the rate constant for the interconversion via $TS2_{ISO}$ is approximately two orders of magnitude larger than those for the addition pathways (TS2c and TS2d) at the relevant temperature. This significant kinetic acceleration confirms that the interconversion between C2a and C2b is indeed much faster than the addition reaction steps. We will list the results in Table S27 in Supplement and add the discussion in the revised article "The five-membered ring species C2a and C2b readily interconvert, as the rate constant for the isomerization process is approximately two orders of magnitude larger than that of the addition reaction (Table S26)." in page 23.

4). There is a good justification for the use of M11L as the lower level of electronic structure theory for the direct dynamics calculations. The authors also have performed thorough benchmarking to validate more affordable electronic structure approaches applicable to larger molecules.

Author response: Thanks for your comments.

5). The authors should briefly describe, on p. 16 or in the Supplementary Information, how they determined the number of conformers for larger aldehydes.

Author response: Thanks for your comments. These conformers were generated using the Mstor 2017 code by rotating the dihedral angles of all reactants and transition states. we will added presentation in the revised article "Conformers for each reactant and transition state were obtained by rotating the dihedral angles listed in Table S10." In page 16.

6). The authors should briefly explain how the (small) falloff factor of 1.34 (p. 18) is determined for the pressure-dependent rate constants in Table S12.

Author response: Thanks for your comments. The falloff factor is from the ratio of is calculated as the ratio of 0.0316 bar (at 298 K) to 1000 bar. we will add presentation in the revised article "For example, the falloff factor calculated for the CH_2OO + HCHO reaction at 298 K and 0.0316 bar is 1.34 (Table S13). This factor, defined as the ratio of the rate constant at 1000 bar to that at 0.0316 bar, indicates only a weak pressure dependence for this system. This result is in excellent agreement with the findings reported by Luo et al. (Luo et al., 2023)." in Table S18.

7). The observation that, based on their atmospheric modeling, atmospheric CH_2OO concentrations are lowered far more than aldehyde concentrations (Figure 5) is helpful. It is also commendable that the authors refrain from overselling the atmospheric significance of their predicted rate constants.

Author response: Thanks for your comments.

Presentation quality

The authors provide a solid, concise introduction that does a good job of motivating the research.

The authors assume too much familiarity with the theoretical details of their research. This makes parts of the current version of the manuscript not approachable for the large majority of atmospheric chemists who read *Atmospheric Chemistry and Physics*. I recommend the following improvements:

(1). Brief definitions and/or explanations of topics like anharmonicity, re-crossing, the dual-level strategy for calculating rate constants, and the multi-structural anharmonic factor (equations 5 and 6).

Author response: Thanks for your comments. We will add relative explanation in Table A1 of Supplement.

(2). There needs to be a literature reference for the MW2-F12.L scheme, along with a brief description of what the scheme achieves.

Author response: Thanks for your comments. We will add the reference about MW2-F12.L scheme in Table S9 of Supplement.

(3). Equation 2, which presents the basis set extrapolation scheme, must be unpacked; the notation is obscure.

Author response: Thanks for your comments. We will add the explanation "with L=2 for cc-pVDZ and 3 for cc-pVTZ and VTZ(d)."

(4). There appears to be an error in the color scale for the rightmost map in Figure 5. I think the color scale is reversed: most of the world appears white, which should mean that there is virtually no change in predicted sulfate concentration in spite of the predicted faster rate constant for the CH_2OO + HCHO reaction.

Author response: Thanks for your comments. We will amend this error in the revised article.