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Title: "Reactions of Carbonyl Oxide with Aldehydes: Accurate Electronic Structure Methods, Kinetic Insights, and Atmospheric Implications"
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Responses in blue.

RC1

Xie and Long have used a diverse combination of computational methods to study the reaction of carbonyl oxide (CH_2OO) with a series of aldehydes, and implemented key results in a chemistry-transport model to assess the atmospheric implications. Overall, the manuscript is well written, and the combination of methods used is appropriate to the task. I'm thus happy to recommend publication, subject to some very minor revisions.
Questions to the authors and/or suggestions for further improvement:

1)The authors perform their most accurate calculations for reaction 1, H_2COO + HCHO, and also use these results to "anchor" predictions on other reactions (as per the last term in their equation 3). However, as noted in the discussion on page 20, the computational results at 296 K are still 7.3 times higher than the most recent experimental rate. Can the authors comment on possible reasons for this? According to Figure 4, the experimental and computational temperature dependence is also quite different - can this be used to narrow down the source of the discrepancy? Also, given the so-far unresolved discrepancy, the repeated use of phrases like "quantitative accuracy", "underscoring the reliability of our calculated results" (and so on) is perhaps a bit overstated, maybe rephrase a few of these instances.

Author response: We thank the reviewer for raising this important point regarding the discrepancy between theoretical and experimental rate coefficients for the CH_2OO + HCHO reaction. We agree that a noticeable deviation exists between theoretical predictions and available experimental data. At present, it is not entirely clear whether this discrepancy originates primarily from experimental uncertainties or from remaining limitations in the theoretical description.

From the theoretical side, we have carefully examined all factors that could significantly influence the predicted kinetics: Geometric optimization and frequency calculations have been performed using the currently most precise method—CCSD(T)F12a/cc-pVTZ-F12, and the singlet-point energy were characterized using high-level coupled-cluster methods with systematic treatment of basis set convergence and higher-order correlation effects. The computed energetics approach the practical limit of coupled-cluster theory and are expected to be close to the Full CI limit within chemical accuracy. Zero-point energy corrections and thermal contributions were consistently included. All accessible reaction pathways, including pre-reactive complexes, post-reactive complexes, and possible barrierless addition channels, were explored. No energetically competitive alternative channels were identified that would substantially alter the overall rate constant. The rate coefficients were calculated using dual-level strategy which including canonical and variational transition state theory where appropriate, including tunneling, recrossing, anharmonicity, and torsional anharmonicity corrections. Despite this comprehensive treatment, the discrepancy with experiment persists.

We therefore consider two plausible explanations: The experimental determination of CH_2OO

kinetics may introduce systematic uncertainties. Alternatively, subtle dynamic effects beyond conventional transition state theory (e.g., non-statistical dynamics or complex-forming behavior) may play a role and require further investigation.

2)Please add a reference to the MW2-F12.L scheme when it is mentioned on page 7.

Author response: Thank you for your comments. We have now added the appropriate reference describing the MW2-F12.L scheme in the Supplement.

3) In the discussion on section 2.1., please briefly describe the main differences between W3X-L and GMMQ.L4, and if possible comment on the origin of the 0.24 kcal/mol deviation. The latter goes up to CCSDTQ while the former goes to CCSDT(Q), but given the very small CCSDTQ - CCSDT(Q) contribution this is probably NOT the major source of the deviation (as already noted by the authors on page 14 - basically I'm asking them to elaborate a bit on the "differences between the MW2-F12.L and W2X components" mentioned there).

Author response: Thanks for your comments. The difference between W2X and MW2-F12.L will be listed in Table S7 and S8 in the Supplement. We will rephase the description in the revised article "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.

4)The discussion in section 2.1 mainly concerns the convergence of results with respect to the level of correlation (highest number of excitations) in the coupled cluster method. This is understandable, as this aspect is the most novel part of the work. However, I note that all the "post-CCSD(T)" corrections are computed with very modest basis sets. (Again, understandable given the demonstrated rapid basis-set convergence of these corrections). Nevertheless, a brief recap of the employed basis set extrapolation (presumably performed at lower levels of theory in the MW2-F12.L scheme) could be helpful to readers. How large basis sets are used to extrapolate e.g. the HF or CCSD or CCSD(T) energies? This question is also related to point 1 above - what remaining error sources could possibly explain a discrepancy of a factor of 7.3…?

Author response: Thanks for your comments. We will added Table S7 to the Supplement, which provides comprehensive details of the MW2-F12.L scheme, including the specific basis sets used for each energy component. Specifically, we will highlight that MW2-F12.L utilizes significantly larger basis sets compared to the W2X protocol, whilst also accounting for nuclear charge corrections. The 7.3-fold difference may not originate from the basis set used in this work. We will performed the discussion "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.

5)"Precreation" on line 240 (page 15) should presumably be "pre-reaction".

Author response: Thanks for your comments. We will corrected this problem.

6)"Barrierless barrier process" on line 340 (page 22) should presumably read just "Barrierless process".

Author response: Thanks for your comments. We will corrected this problem.

7)Do the "base-version model simulations" mentioned on line 420 (page 23) refer to the GEOS-CHEM simulations performed in this study, or to something else? Please clarify.

Author response: Thanks for your comments. The "base" model using default setting were clarified in 2.5. Atmospheric modeling section.

8)Please explain why the four specific regions/areas in Table 6 were selected. Are these representative for various chemical regimes in the atmosphere, or what is the reasoning?

Author response: Thanks for your comments. These four regions were selected owing to their significant concentration differences in CH_2OO/OH.

9)Moderate (6-12%) reductions in "gas-phase sulfate" (presumably meaning gas-phase sulfuric acid, as sulfate ions are not even stable in the in the gas phase - I do understand the phrasing may originate from the GEOS-CHEM model) were observed in Arctic/sub-Arctic regions during night due to CH2OO depletion. This is interesting - but to assess the implications better, it would be good to know what the absolute H2SO4 concentrations or production rates are in these conditions. A 10% reduction in a number that is already too small to matter is not very impactful, while a 10% reduction of a substantial number is much more important. Please elaborate on this.

Author response: Thanks for your comments. The PH_2SO_4 here refers to gas-phase sulphate, which in GEOS-Chem primarily originates from the gas-phase oxidation of SO_2. Its maximum concentration globally can reach 10^8, and we will depict its concentration in the base version in Figure S10. We also mentioned in the revised article "We found that the concentration of gas-phase sulfate can reach 10^8 molecules cm^{-3} in Mexico region in Figure S10." On page 26.