Response to the Reviewer's Comments

October 7, 2025

1 REFEREE REPORT

Comment: As pointed out by the first reviewer the present work only suggests that the Criegee + HONO reaction is the dominant sink of Criegee for $(CH_3)_2COO$ and not at all for CH_2OO. And even for $(CH_3)_2COO$ it is only dominant at best at temperatures below 225 K. For CH_2OO, Fig. 3 shows that the CH_2OO + SO_2 reaction is always a larger sink than the title reaction. For $(CH_3)_2COO$, the unimolecular loss is the dominant sink except perhaps below 225 K. The authors need to make a much more serious effort to remove all of their overstatements. For example, the title needs to be revised, the concluding statements need to be further revised, and the plot in Fig. 4 must include the unimolecular loss rate. The authors must reread the whole manuscript to make sure that any such overstatements have been removed. It is important for a paper to have a correct physical interpretation and tone in addition to correct data.

Reply: We agree with the reviewer that HONO acts as a sink for $(CH_3)_2COO$, but not for CH_2OO. We further acknowledge that HONO is dominant sink of $(CH_3)_2COO$ at temperatures below 225 K. In the revised manuscript, we have updated Figure 4 to include the unimolecular rate of $(CH_3)_2COO$. In the revised manuscript, we also make sure that from title to conclusion our language represent the real picture rather any overstatement.

Comment: The authors need to either improve their discussion of why they believe the M06-2X/aug-cc-pVTZ is an effective approach for determining the stationary point geometries and vibrational frequencies, or simply remove all of that discussion. An error in the geometry of 0.04 Å converts to a 2 kcal/mol error for a typical force constant of 2000 N/m. Is that what the authors deem an appropriate error for an accurate geometry? Similarly, an error of 250 cm-1 in the frequency correlates with anywhere from a

few % error to a factor of two or more error in the partition function (depending on which frequency is in error by that amount). Is a factor of two error in the rate prediction an indication that the method is adequate for kinetics calculations? And that is for just one vibrational mode. What is the cumulative effect of such errors for many modes? Oddly, I actually believe that the M06-2X/aug-cc-pVTZ is a suitable enough method for predicting the kinetics for this reaction, but the authors arguments are so poorly presented that one can readily come to the opposite conclusion. A correct statement would be that, prior literature studies suggest 2sigma uncertainties of $\sim$ 2 kcal/mol in CCSD(T)/CBS//M06-2X barrier heights and factor of two sorts of uncertainties in partition function ratios. It would be much better to simply say something like that.

Reply: We thank the reviewer for the suggestion. In the revised manuscript, we simply state that the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory, was chosen based on previous studies where this level of theory was found to be reasonable in similar reaction.

Comment: The description of the VTST calculations with KTOOLS is missing key details. Ordinarily a VTST calculation requires some description of both the potential energies along some form of a minimum energy path and the vibrational frequencies for the orthogonal motions along the reaction path. The latter are not described at all. Furthermore, the authors provide no indication of the electronic structure method that was used to map the PES. Nor do they describe the method used to scan the PES – is it some sort of distinguished reaction coordinate analysis?

Reply: In the revised manuscript, we have provided the details of the VTST calculations. The minimum energy path (MEP) was obtained by manually scanning along the reaction coordinate, with geometries optimized at the M06-2X/aug-cc-pVTZ level of theory using Gaussian 16. Single point energies at each point were improved at the CCSD(T)/CBS level. The vibrational frequencies orthogonal to the reaction coordinate were computed at each point along the MEP and employed in the VTST using the KTOOLS package. These frequencies are provided in Table S9 of the ESI.

Comment:The ILT for the reaction from the PC to the products also needs some description of the presumed temperature dependence.

Reply: In the revised manuscript, now we have mentioned that for ILT, the rate constants are assumed to be independent of temperature. (on page 4 on line 115)

Comment: It's nice to know that the torsional scans did not find lower global minimal conformers. Nevertheless, some description should still be provided regarding how extensive your search for conformers was initially. Was some manual search of the conformational space performed? Did you just accept whatever conformer was first found?

Reply: We performed both, an automated scan and a manual search, for lower energy conformers using the Gaussian 16 package. All conformers were fully optimized at the M06-2X/aug-cc-pVTZ level of theory, and their single point energies were computed at the CCSD(T)/CBS level. Among these, no conformers were found with energies lower than that of the reported conformer. Now we have mention it in the revised manuscript. Therefore, we believe that the reported conformer represents the global minimum.

Comment: Why would the L-J parameters for a CH_2OO–HONO complex correspond to the average of those for CH_2OO and HONO. Shouldn't they correspond more closely to some sort of sum of the parameters. Certainly the size of the complex is not the average of the individual sizes of the components. This treatment should be revised and the master equation calculations repeated.

Reply: We agree with the reviewer. In the revised manuscript, we have fitted the Lennard-Jones (L-J) parameters. These parameters are used to describe the collisional interactions with the bath gas. To obtain them, we performed a bond distance scan between the reactive complex (RC) and the bath gas molecule, and subsequently fitted the interaction energy with the bond distance in the Lennard-Jones potential. The fitted plot provided the corresponding L-J parameter values.

Comment: On. p. 5 – why do you describe the reaction as occurring in two steps? Isn't it three steps – formation of RC1, passage through TS1 to form PC1, then decomposition of PC1 to products. This proper physical description as three steps is important because there may be some stabilization of PC1. On a related note, the authors should mention whether or not there is there any stabilization of either reactant or product complexes? With 45 kcal/mol exothermicity and 27 kcal/mol bond dissociation energies there is particularly some possibility of the product complexes being stabilized.

Reply: In the revised manuscript, we have mentioned that the reaction is a three step process. The product complex is $\sim$ 44.70 kcal mol^{-1} stable with respect to the isolated reactants, while the bond dissociation energy required to convert the PC into the final isolated product is $\sim$ 27.4 kcal mol^{-1}. In addition we have computed Gibbs free energy profile of the reaction at 298 K, (Figure S2 of ESI). The Gibbs free energy profile suggests that the isolated products are $\sim$ 2.5 kcal mol^{-1} lower in free energy relative to the PC.

Comment: On line 146 RC should be RC1. On Line 158 RC should be RC2.

Reply: In the revised manuscript, we have corrected "RC" to "RC1" on line 146 and to "RC2" on line 158.

Comment: The capture rates reported in Table S3 are still smaller than I would have naively guessed by about a factor of 4. This is likely an artifact of some limitation in the VTST calculation, but since those are not described in appropriate detail it is hard to judge what the issue is.

Reply: We agree with the reviewer that the capture rate may be faster than our calculated value. The capture rate is rate determining step and essentially at collision limit. The VTST calculated rate is sensitive to the the minimum energy path scan points. So this could be artifact of VTST. We have mention the details of VTST (energy and frequency) on Table S9 of ESI.

Comment: A proper citation (i.e., likely to one of his websites) should be provided to the actual source of the Ruscic et al. thermochemical values for the reaction energy.
Reply: In the revised manuscript, we have added the appropriate citation to the official Active Thermochemical Tables (ATcT).

Comment:It appears that the rate calculations were performed without the CCSDT(Q) correction. Why? Do the authors somehow believe that including that correction would not improve the accuracy of the predictions. If so, they should state that.

Reply: Due to the limited computational facilities, we were able to perform CCSDT(Q)/CBS calculation only for the simplest Criegee not for the dimethyl substituted Criegee. In the revised manuscript, for simplest Criegee, we have compare the rate constant estimated at CCSDT(Q)/CBS PES with CCSD(T)/CBS values to estimate the uncertainty in rate constant due the multi-reference nature of reaction. Our post-CCSD(T) corrections are below 1 kcal mol^{-1} and the estimated rate constants are also similar. For example, at 298 K, the bimolecular rate constants calculated at the post-CCSD(T) and CCSD(T)/CBS levels are 5.53×10^{-12} and 7.21×10^{-12} cm^3 molecule^{-1} sec^{-1}, respectively.

Comment: The discussion of the uncertainties on p. 6 lacks any discussion of the uncertainties arising from inadequate partition function evaluations. I would estimate that such uncertainties are at least a factor of two and probably more like a factor of 4. Indeed, as I mention above, I expect that the true capture rate would probably be a factor of four larger, and almost certainly a factor of two larger. It appears that their uncertainty analysis does not consider the uncertainties in this capture rate. Furthermore, I strongly suspect that the barrier height 2 sigma uncertainties are more like 2 kcal/mol. Also, since the more relevant part of the prediction is for low temperature, they should indicate how the uncertainties change with decreasing temperature.

Reply: We agree with the reviewer. In the revised manuscript, we have included 2σ ($\pm$ 2 kcal mol^{-1}) uncertainties in the error analysis of the rate constants. Accordingly, we have also added a discussion of the uncertainties arising from the partition function evaluations. This discussion has been incorporated into the revised manuscript (on page 6 on line 192).

Comment: The paragraph on p. 7 starting on line 219 first misleads the reader to think that the CH_2OO + HONO is dominant at combined low temperature and low RH and then corrects that to indicate that CH_2OO + SO_2 is always dominant over CH_2OO + HONO. Just start off with the proper statement that CH_2OO + HONO is never the dominant sink, or even major sink (it looks like the maximum is about 20% at about 240 K and low RH). Then the details can be discussed. That is the proper primary finding of your calculations and the more clearly it is stated the better.

Reply: In the revised manuscript, we have rectified our statement and revised the manuscript accordingly. *"In Figure 3, we have compared the* k_{eff} *of* CH_2OO *+ HONO with the* k_{eff} *of* $CH_2OO + H_2O/(H_2O)_2/SO_2$ *reactions. Figure 3 shows, HONO is not a major sink of* CH_2OO*. It is evident from Figure 3 that at 100% RH,* k_{eff} *of* $CH_2OO + (H_2O)_2$ *is the dominant reaction across the entire temperature range (213–320 K). As far* *as CH_2OO + SO_2 reaction is concerned, its k_{eff} values are $\sim$ 5 times higher than that of CH_2OO + HONO reaction within the whole temperature range. At 20% RH, k_{eff} for CH_2OO + $(H_2O)_2$ and CH_2OO + H_2O remain dominant at higher temperatures, specifically within 235–320 K and 260–320 K, respectively. However, at lower temperatures, k_{eff} of CH_2OO + HONO becomes dominant, surpassing both, CH_2OO + $(H_2O)_2$ and CH_2OO + H_2O in the range of 213–235 K and 213–260 K, respectively. It is indicating that CH_2OO + HONO reaction is a minor contributor compared to the other sinks of Criegee intermediates.“*

Comment: Table S6 is central to the authors argument that the HONO + $(CH_3)_2COO$ is the dominant sink at low temperature. Their data for the unimolecular dissociation of $(CH_3)_2COO$ in that Table needs some citation as to the source of the data. That data also needs to be directly plotted in Fig. 4. Then the discussion of Fig. 4 on p. 8 should again start with the primary conclusion that only below 225 K is the $(CH_3)_2COO$ + HONO reaction predicted to be the dominant sink of $(CH_3)_2COO$. Then more details can be provided.

Reply: We thank the reviewer for the suggestions. In the revised manuscript, we have cited the relevant Table and modified Figure 4 to include the unimolecular rate. We also corrected our statement on page 8 as follows: *"It is evident from Figure 4 that at temperatures below 225 K, HONO is the dominant sink for $(CH_3)_2COO$. At temperatures above 225 K, unimolecular dissociation becomes the major sink. As far as bimolecular sink of $(CH_3)_2COO$ is concerned HONO can be a major sink for $(CH_3)_2COO$. It is evident from Figure 4 that at 100% RH, k_{eff} of $(CH_3)_2COO$ + HONO can dominate over k_{eff} of $(CH_3)_2COO$ + H_2O and $(CH_3)_2COO$ + $(H_2O)_2$ for a relatively wider range of temperatures. For example, the dominant temperature range of $(CH_3)_2COO$ + HONO is, 213–275 K for $(CH_3)_2COO$ + $(H_2O)_2$ and 213–290 K for $(CH_3)_2COO$ + H_2O. At 20% RH, k_{eff} of $(CH_3)_2COO$ + HONO becomes dominant over k_{eff} of both, $(CH_3)_2COO$ + H_2O and $(CH_3)_2COO$ + $(H_2O)_2$ in almost whole temperature range (213–310 K). For example, at 298 K, k_{eff} of $(CH_3)_2COO$ + HONO is $\sim$ 1.8 sec^{-1}, which is 1.6 times and 2.2 times higher than the same for $(CH_3)_2COO$ + H_2O and $(CH_3)_2COO$ + $(H_2O)_2$, respectively "*

Comment: Again, the statement in the conclusion “By comparing it with other known sinks of CI, we have shown that this reaction can serve as a major sink for Criegee intermediates in most of the atmospheric conditions” is not in fact true.

Reply: We correct our statement in the revised manuscript. *"By com-*

paring it with other known sinks of CI, we have shown that HONO can serve as a major bimolecular sink for bigger Criegee intermediates ($(CH_3)_2COO$) and minor contributor at low humidity and low temperature for simple CH_2OO."

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Comment: Unfortunately, the relevant articles are still missed such as J. Am. Chem. Soc. 2016, 138, 14409-14422. and J. Am. Chem. Soc. 2021, 143, 8402-8413.

Reply: We thank the reviewer's careful assessment. We have now cited them appropriately in the revised manuscript.