Response to the Reviewer's Comments

August 1, 2025

1 REFEREE REPORT

Comment: The atmospheric lifetimes of CH_2OO with water dimer had been detailedly investigations from theoretical and experimental methods. Please read the reference (J. Am. Chem. Soc. 2021, 143, 8402-8413). The atmospheric lifetime is 2.12×10^{-4} sec at 0 km in Table 7 in J. Am. Chem. Soc. 2021, 143, 8402-8413. Although the atmospheric lifetime of CH_2OO with water dimer is very long in the stratosphere, the concentrations of Criegee intermediates are very low at altitude above 15 km. Therefore, the importance of Criegee intermediates occurs in the troposphere. According to Table 1 in the present work, I assume that the concentration of HONO is about 10^{10} molecules cm^{-3} in the troposphere, which leads to the atmospheric lifetime of CH_2OO with HONO is about 10^2 sec. This shows that HONO does not make any contribution to the sink of CH_2OO. In addition, Criegee intermediates are mainly produced from the ozonolysis of BVOCs, while HONO is mainly produced at urban regions.

Reply: We agree with the reviewer that under high humid condition, HONO is not a major sink for simple CH_2OO in the atmosphere; rather, it plays a dominant role in the removal of substituted Criegee intermediates, i.e., $(CH_3)_2COO$. This is clearly illustrated in Figure 3 and 4 of the main manuscript. It is evident from Figure 3 that at 100% relative humidity (RH), the reaction of CH_2OO with $(H_2O)_2$ is dominant across the entire temperature range studied (213–320 K). But it is important to mention that the concentration of $(H_2O)_2$ as well as H_2O greatly depends on the relative humidity (RH) and temperature. For example, at 20% RH, the effective rate constant (k_{eff}) for CH_2OO + HONO becomes comparable to the same for CH_2OO + $(H_2O)_2$ and CH_2OO + H_2O reactions in the lower temperature ranges of 213–235 K and 213–260 K, respectively. This suggests that although CH_2OO + HONO is a minor sink under typical tropospheric conditions, it can become relevant under specific atmospheric conditions. We

have discussed it in the revised manuscript on page 7.
For the second concern of the referee regarding the sources of Criegee and HONO, it is worth mentioning that simpler Criegee intermediates (those Criegee which has less than four carbon atoms) are produced from the both sources, i.e. ozonolysis of biogenic volatile organic compounds (BVOCs) in forested environments and from anthropogenic sources in urban areas. For example, CH_2OO (formed from 23 VOCs) has 20% production from anthropogenic sources and 19% from biogenic sources. Similarly, $(CH_3)_2COO$ (formed from 10 VOCs) has 28% anthropogenic production and 9% biogenic production. Thus, the two Criegee intermediates selected in the present work are representative of species emitted from both biogenic and anthropogenic sources. We have added a short discussion of it in the conclusion of the revised manuscript. As far as HONO is concerned, although HONO is primarily generated in urban regions, several field measurements have reported a reasonable HONO concentrations ($\sim 10^8$ to 10^{10} molecules cm^{-3}) even in forested areas[6, 1, 10, 18, 5, 15, 11, 12, 19].

Comment: The second issue is computational methods. In fact, there are dozens of papers that have shown that post-CCSD(T) calculations are required to obtain quantitative barrier heights for the reactions including Criegee intermediates. Although I have to admit the introduction of the calculations will extremely increase the computational costs, it should be clearly explained and reviewed in the present progress. This is very helpful for potential readers to know the progress. Please read these articles (J. Am. Chem. Soc.2025, 147 (14), 12263-12272.; Atmos. Environ. 2025, 341, 120928.;Research 2024, 7, 0525.; Fundam. Res. 2024, 4 (5), 1216-1224.; Proc. Natl. Acad. Sci. USA 2018, 115, 6135-6140. And so on).

Reply: As indicated by the reviewer, post-CCSD(T) calculations are indeed computationally very demanding. Still, to assess the uncertainty in the energetics due to the exclusion of post-CCSD(T) corrections, we have carried out CCSDT(Q)/CBS calculations for the smaller Criegee intermediate reaction (CH_2OO + HONO). We have focused on key stationary points, i.e., the reactant complex (RC) and transition state (TS). The different components of post-CCSD(T) corrections (δ_T and $\delta_T(Q)$) are provided in Table S7 of the ESI. It is evident from Table S7 that post-CCSD(T) corrections have made only minor changes in the calculated energetics of the CH_2OO + HONO reaction. In fact, post-CCSD(T) corrections have reduced the stabilization energy of RC by only $\sim$0.54 kcal mol^{-1}; on the other hand, they have raised the barrier height by a similar amount, i.e., 0.67 kcal mol^{-1}, which lies within the chemical accuracy. This suggests that our CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory is both reliable and

computationally efficient for studying the title reaction. To further confirm this, we have also computed the rate constants using the post-CCSD(T) level energetics and found negligible changes in the rate constant of CH_2OO + HONO reaction. For example, at 298 K, the rate constant decreased slightly from $\sim 7.2\times10^{-12}$ cm^3 molecule^{-1} sec^{-1} to $\sim 5.5\times10^{-12}$ cm^3 molecule^{-1} sec^{-1}. This further supports the reliability of our computational approach. We have discussed it in the revised manuscript on page 6 and line 180.

Comment: In kinetics calculations, there are still lots of factors that do not consider such as recrossing effects, torsional anharmonicity, and anharmonicity. In addition, the low energy barrier, what is the rate-determining step. I guess that the formed pre-reactive complex is the rate-determining step like Criegee reaction with HCOOH, Therefore, VRC-TST is necessary for the barrierless process.

Reply: The reviewer is right that in the title reaction, the formation of the pre-reactive complex is the rate-determining step. Since this step is barrierless, a variational treatment is essential for obtaining accurate rate coefficients. To account for this, we have employed KTOOLS code as implemented in MultiWell suite of programs, which uses variational transition state theory (VTST) for the barrierless association process. The inputs for the KTOOLS are potential energy surface scans along the coordinate describing the dissociation of RC to isolated reactants. Therefore, a variational approach is explicitly incorporated in our kinetic calculations for the initial step. We have now added few lines in the manuscript to make it more clearer. In fact, this methodology is consistent with previous studies on bimolecular reactions of Criegee intermediates, where similar kinetic treatments have been successfully applied [17, 8, 4, 3, 13, 7, 9, 14, 16, 2]. In addition, in the revised manuscript, we have also included a deterministic eigenvalue-eigenvector-based approach, specifically the Bartis-Widom method (implemented in MESMER program) to estimate rate constants. In addition, to account for torsional anharmonicity, we have also performed a relaxed potential energy scan of the torsional rotation along N–O bond of HONO moiety. The resulting torsional potential has been used to model hindered internal rotation (HIR). This correction led to negligible changes in the calculated rate constants. We have added the details of it on page 4.

Comment: Lines "Our study also suggests that HONO has the potential to become the most dominant sink of Criegee intermediate, surpassing SO_2 and water dimer, even in high humid condition", it is not validated.

Reply: We agree with the reviewer that this statement is not valid for

all types of CI + HONO reaction. In fact, we made this statement for our substituted $(CH_3)_2COO$ + HONO reaction. In Figure 4 of the manuscript, it can be clearly seen that the k_{eff} of $(CH_3)_2COO$ + HONO reaction is dominant over almost the entire temperature range, even in the presence of $(H_2O)_2$ at RH 100% and SO_2. Therefore, this statement is quite valid for the dimethyl-substituted Criegee intermediate but not for all the Criegee intermediate. Now in the revised manuscript, we have corrected that statement in the abstract.

Comment: Lines "the bimolecular reaction paths can be the main sink of sCI (Osborn and Taatjes, 2015; Lin et al., 2015; Sheps et al., 2014; Vereecken and Francisco, 2012)." Some important key references have been missed such as . J. Am. Chem. Soc. 2016, 138, 14409-14422. and J. Am. Chem. Soc. 2021, 143, 8402-8413.

Reply: Thanks for the references. These references was indeed helpful. As per the reviewer's advice, we have duly cited these references in the revised manuscript.

Comment: Kinetics methods should be moved into computational section.

Reply: As per the reviewer's advice, we have now moved the kinetics methods to the methodology section of the revised manuscript.

Comment: It needs to add some tables for showing the atmospheric lifetimes of Criegee intermediates with H_2O, $(H_2O)_2$, SO_2, HCOOH, and HONO as the function of altitude.

Reply: Unfortunately, we could not find any literature containing relevant data on HONO concentrations as a function of altitude (perhaps due to difficulty in the field measurements). Therefore, we have avoided estimating altitude-dependent lifetimes of Criegee intermediates with HONO.

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Comment: The description of their rate calculations seems to imply that they evaluate the overall rate constant as a product of a separately calculated rate for the formation of RC1 and a master equation calculation for the branching in the thermal dissociation of RC1 (between forward reaction, kuni, and back dissociation to reactants). This product of terms would be appropriate if RC1 was being formed in the high pressure limit. But it most certainly is not. In this case, the master equation should instead be used to directly obtain the rate constant for proceeding from the reactants to the bimolecular products.

Reply: As per the reviewer's suggestion, we have now employed a traditional master equation approach using MESMER software package to estimate the rate constants. In the revised manuscript, we have provided MESMER-based calculations, where pseudo-first-order rate constants are determined directly from the reactants to the isolated products using the master equation method. The rate constants obtained from MESMER are provided in Table 1 of the revised manuscript.

Comment: There is also some possibility that the PCi complexes are collisionally stabilized since they are fairly deep wells on their PESs. Such stabilization would be important as it would reduce the rate of forming OH. Thus, properly formulated master equations should include the PCi complexes and some rate for their decomposition.

Reply: In the revised manuscript, we have now added the reaction path from the product complex (PC) to the isolated products in the rate constant calculations using MESMER software package. The estimated effective forward rate values after incorporating PC $\rightarrow$ isolated products step comes out to be almost same compared to the previous one (without adding this step).

Comment: The authors refer to a KTOOLS code for estimating the formation rate. The authors should also briefly describe the physical assumption behind the calculation in KTOOLS. This point is significant because their formation rates appear to be about an order of magnitude less than what would be expected.

Reply: We agree with the reviewer that special care is needed in estimating the RC formation rate constant, as this is the rate-determining step. Since this association step is barrierless, a variational treatment is essential for obtaining accurate rate coefficients. To account for this, we have employed KTOOLS code as implemented in the MultiWell suite of programs, which uses variational transition state theory (VTST) for the barrierless reaction. The inputs for KTOOLS are potential energy surface scans along the coordinate describing the dissociation of RC to isolated reactants. Each point on the potential energy surface serves as a trial transition state; KTOOLS searches for the transition state for which the reaction flux is minimized. To address the referee's concern, in the revised manuscript, we have refined the potential energy surface scan for this step. The reviewer is correct that the RC formation rate now becomes one order of magnitude higher compared to the previous work. We have now added a brief discussion of this on page 4 of the revised manuscript.

Comment: The wells and TSs (and perhaps the reactants) appear to have hindered rotational modes, some of which might have multiple distinct minima. At the very least, the authors should describe how they treated those torsional motions, and whether or not they searched for multiple torsional minima to ensure they had found the global minimum conformational states.

Reply: We agree that the reactant complex (RC) and transition state (TS) have hindered rotational motions, and there may be multiple conformations due to different torsional angles. To take this into account, we have used HinderedRotorQM1D model in the MESMER software to compute the rate constants. Specifically, we performed a one-dimensional potential energy scan of OH torsion along the N–O bond in both the RC and TS. The scan covered the full 0° to 360° range. The resulting energy profile was used to calculate the hindered rotor partition functions. During this scan, we found local minima in both the RC and TS, which suggests that our originally optimized structures correspond to the global minimum conformers. After incorporating this hindered rotor correction, the computed rate constants are found to be almost same compared to rigid-rotor harmonic oscillator (RRHO) treatment, which indicates that torsional anharmonicity has minimal impact on the overall kinetics for this system. We have added

the details of it on page 4 line 121.

Comment: It appears that the TS energy reported here for CH_2OO + HONO is about 8 kcal/mol below what was reported in an earlier report from the same group. This is rather odd since the electronic structure methods are very similar. Should I presume that the uncertainty in the energy is truly that large. Some comment on this discrepancy is needed, and ideally the authors would provide some indication of the expected uncertainty in their energies.

Reply: The previous study investigated a different path of the same reaction (that lead to HPMN product). Therefore, the TS of previous study is different from that found in the present work. As a result, the calculated barrier height in the present work is differing ($\sim$ 8 kcal mol^{-1} lower in energy). However, to further check for uncertainty in the energetics, we have carried out post-CCSD(T) calculations (CCSDT(Q)/CBS) for the smaller Criegee intermediate reaction i.e., CH_2OO + HONO reaction, focusing on key stationary points, i.e., RC and TS. The obtained post-CCSD(T) corrections have made only minor changes in the calculated energetics of CH_2OO + HONO reaction. In fact, post-CCSD(T) corrections have reduced the stabilization energy of RC by only $\sim$ 0.54 kcal mol^{-1}; on the other hand, they have raised the barrier height by a similar amount, i.e., 0.67 kcal mol^{-1}, which lies well within the range of chemical accuracy.

Comment: It is well known that CH_2OO has significant multireference character that often disappears in the TSs for its reaction. This commonly results in about a 1 kcal/mol raising of the barrier heights relative to CCSD(T)/CBS estimates. Some comment on this shortcoming in their estimates would be helpful.

Reply: We have dealt with this problem in two ways. First, we have employed a well-established specialized method for multireference systems, i.e., incorporating post-CCSD(T) corrections to validate the energetics. Second, we have performed an uncertainty analysis by taking $\pm$ 1 kcal mol^{-1} uncertainty in the reaction barriers as well as well depths (detailed discussion can be found on page 6 and line 175 of the revised manuscript). Both of these approaches introduce only slight changes in the rate constants, which suggests that energy uncertainty due to the multireference character of Criegee intermediates is not going to alter the overall conclusions of the present work.

Comment: The authors claim that 0.04 angstrom geometry errors clearly suggest that M062X geometries are accurate. For this statement to be true, the authors should provide some estimate of how large an error could arise from such bond length errors.

In principle, that is straightforward from some consideration of typical force constants. Simply stating that the geometry errors are small is not helpful. Similarly, the authors claim that 250 cm-1 frequency errors imply that M062X is appropriate for frequency calculations. From my experience, those sorts of frequency errors are extraordinarily large, and would make me wonder if I had done something wrong. My expectation is that they could yield order of magnitude sorts of errors in the predicted rates. Some more appropriate discussion of the meaning of those shortcomings is needed.

Reply: To address the reviewer's concern, we have calculated the uncertainties associated with the computed rate constant due to an error of 250 cm^{-1} ($\sim$ 0.7 kcal mol^{-1}) in the energetics of the reaction. We have assumed this much uncertainty ($\pm$ 1 kcal mol^{-1}) in well depths as well as in reaction barriers and estimated uncertainty in the rate constants at 298 K for simple Criegee + HONO reaction. Due to $\pm$ 1 kcal mol^{-1} uncertainty in the reaction barriers and well depths, the maximum deviation in the rate constant is $\sim 7.21^{+4.67}_{-3.65} \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} ($\pm$1 reaction barriers) and $\sim 7.21^{+0.45}_{-0.45} \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} ($\pm$1 well depths), respectively. It suggests that this much of uncertainty is not going to affect the overall conclusion of the present work. We have discussed this point on page 6 and line 187 of the revised manuscript.

Comment: The focus on just the bimolecular rate constants in their discussion of the effective rate constants is misleading. For the $(CH_3)_2COO$ case, the unimolecular decomposition rate near room temperature is about 400 sec^{-1}, which swamps their effective bimolecular rates. With that in mind, their suggestion that the CI + HONO reactions are the major sink for the CI requires some indication as to how rapidly the unimolecular decay rates decrease with temperature.

Reply: The reviewer is right that the unimolecular rate of $(CH_3)_2COO$ is higher at room temperature, i.e., $\sim$ 276 sec^{-1}. But it is important to mention that the unimolecular rate increases rapidly with temperature, whereas for the bimolecular reaction $(CH3)_2COO$ + HONO, k_{eff} increases only slightly. As a result, at lower temperatures, k_{eff} becomes comparable to the unimolecular dissociation rate of $(CH3)_2COO$. For example, at 213 K, k_{eff} and unimolecular rate constants are 3.80 sec^{-1} and 1.82 sec^{-1}, respectively. A comparision between k_{eff} and unimolecular dissociation rate constant of $(CH_3)_2COO$ within 213–320 K is provided in Table S6 of the ESI. It is evident from Table S6 that under conditions of high HONO con-

centration and low temperature, the bimolecular reaction of $(CH_3)_2COO$ with HONO competes well with its unimolecular dissociation. We have included this discussion in the revised manuscript on page 8 and line 251.

Comment: It would be helpful to have some estimate of the expected uncertainty in their rate predictions.

Reply: As per the referee's suggestion, we have added a discussion on the uncertainties associated with the computed rate constant on page 6 of the main manuscript.

Comment: The actual HONO concentration used in their keff calculations should be explicitly stated.

Reply: In the revised manuscript, we have stated explicitly that the concentration of HONO is 8.9×10^{10} molecule cm^{-3}.

Comment: The model simulations are limited enough in scope that I consider them to be highly speculative at best.

Reply: We understand the reviewer's concern about the limited scope of our model simulations. Our primary aim was to provide qualitative insight and mechanistic understanding under a defined set of assumptions and conditions. A more comprehensive study including all Criegee intermediates (CIs), unimolecular, and bimolecular sinks would indeed be necessary for a broader analysis. Such an investigation, however, would require a separate and detailed study. We have included this discussion also in revised manuscript on page 10 and line 319.