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 ~ 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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