Response to the Reviewer's Comments

August 1, 2025

1 REFEREE REPORT

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 → 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 $\mathrm{molecule}^{-1}$ sec^{-1} ($\pm$1 reaction barriers) and $\sim 7.21^{+0.45}_{-0.45} \times 10^{-12}$ cm^3 $\mathrm{molecule}^{-1}$ 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 concentration 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.