

Response to the Reviewer's Comments

July 4, 2026

1 REFEREE REPORT

Comment: On page 2, line 40, the authors mention that the reaction of CIs + HONO is a hydrogen atom transfer (HAT) reaction. However, hydrogen abstraction can also proceed via a proton coupled electron transfer (PCET) mechanism [see for example Chem. Eur. J., 2004, 10:14, 3404-3410, 10.1002/chem.200305714]. I think the authors should provide a citation for this assumption.

Reply: We agree with the reviewer that the hydrogen abstraction (HAT) reaction can also proceed via a proton coupled electron transfer (PCET) mechanism. We have added the appropriate references to support the assumption of the HAT reaction in the revised manuscript.

Comment: Please add citations on page 3, line 63, to both the method and basis set used.

Reply: In the revised manuscript, we have added the appropriate citations for both the method and the basis set used in our calculations.

Comment: In Section 2.2 of the manuscript, the authors define several reaction rate coefficients (k_1 , k_{bi} , k_{uni} etc.), but the values for these are never reported. These should be reported somewhere, as it would help potential readers understand how the final rate constants were derived.

Reply: We thank the reviewer for this valuable suggestion. The individual rate coefficients used in the kinetic calculations, i.e., k_1 , k_{-1} , k_f , k_{bi} , and k_{SSA} are reported in the revised ESI (Tables S11–S14).

Comment: I wonder how realistic it is to use $[\text{HONO}] = 8.8 \times 10^{10} \text{ cm}^{-3}$ at 210 K, as presumably the HONO concentration has temperature dependence. Can the authors comment on how realistic

this is? Does the GEOS-Chem take the temperature dependence into account in some way?

Reply: We agree that the atmospheric concentration of HONO is expected to vary with altitude and temperature. There are two reasons to use the same concentration for the whole temperature range. First the temperature-dependent data available in the literature for HONO concentration are very sparse and have some uncertainty. Second, recent studies have shown that the observed HONO concentration exhibits a C-shaped vertical profile, suggesting that the HONO concentrations in the planetary boundary layer and the upper troposphere are nearly similar. Therefore, we used an average HONO concentration over the entire temperature range. In the GEOS-Chem model, we provided only the temperature-dependent termolecular rate constants. The model calculates the HONO concentration internally, and its temperature dependence is taken into account by the model itself, providing a more realistic concentration temperature dependence.

Comment: The authors calculate effective unimolecular rate constants (k_{eff}) to compare the catalyzed reactions with the uncatalyzed reaction they have investigated. The collision limit k_{coll} between small molecules at room temperature (298 K) is approximately $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Using the same [HONO] value as the authors used, $[\text{HONO}] = 8.8 \times 10^{10} \text{ cm}^{-3}$, the maximal k_{eff} becomes $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \times 8.8 \times 10^{10} \text{ cm}^{-3} = 26.4 \text{ s}^{-1}$. However, the authors report k_{eff} values much higher than 26.4 s^{-1} . These are unphysical, so something is clearly wrong with the kinetic framework (see the next point for one possibility). However, it is hard to evaluate exactly what is going wrong as the individual elementary rate coefficients are not given (see issue 3 above). Another way of approaching this problem is to look at the values reported on page 4, lines 114-116. These reported values (rate coefficients) are approximately within a factor of 60 from k_{coll} (calculated at 298 K). Therefore, I find it highly unlikely that the catalyzed reaction could be over 100 times faster than the uncatalyzed one. The authors should carefully review and address this.

Reply: We thank the reviewer for this important observation. We agree that our previously reported (k_{eff}) values were overestimated. The reason was that we employed the pre-equilibrium approximation for the first step. As a result, the calculated effective rate constants exceeded the physical upper limit imposed by the collision rate. As suggested by the reviewer, in the next comment, to resolve this issue, we have revised the kinetics calculations using the steady-state approximation ($k_{SSA} = k_1 / (k_{-1} + k_f [\text{H}_2\text{O}])$). Now the

k_{eff} values are physically reasonable and remain below the collision limit. In the revised manuscript, we have updated the values accordingly. We have also included the individual rate coefficients used in the kinetic calculations in the ESI (Section 2 of the ESI).

Comment: Closely related to the problem described above is the equation on page 3, line 85. This equation only holds when $k_{-1} \gg k_f$, meaning when the bimolecular complex is more likely to dissociate than further react. However, the CI-HONO complexes seem to be quite strongly bound, especially for the CIs larger than CH_2OO . If detailed balance is used to approximate the rate of dissociation (k_{diss}) for the CI-HONO complexes, one gets $k_{diss} = k_{coll} \times p_{ref} \times \exp[(-dG)/(RT)]$. Then assuming $k_{coll} = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $p_{ref} = 1 \text{ atm} = 2.5 \times 10^{19} \text{ cm}^{-3}$, $T = 298 \text{ K}$, and using the dG value for $(\text{CH}_3)_2\text{COO-HONO}$ (-2.88 kcal/mol , from Figure S2), $k_{diss} = 5 \times 10^6 \text{ s}^{-1}$. This process competes with $k_{coll} \times [\text{H}_2\text{O}]$. Assuming a relative humidity of 100%, at 298 K $[\text{H}_2\text{O}] = 7 \times 10^{17} \text{ cm}^{-3}$, and thereby $k_{coll} \times [\text{H}_2\text{O}] = 2 \times 10^8 \text{ s}^{-1}$. So ultimately it is 40 times more likely that the $(\text{CH}_3)_2\text{COO-HONO}$ reacts with H_2O than for it to dissociate. However, this is the opposite of what is needed for the equation on page 3, line 85, to hold. A possibly better approach to this would be to use the steady-state approximation, which replaces K_{eq} in their equation by $k_1/(k_{-1} + k_f)$. The downside is that this requires explicitly estimating the values of k_1 , k_{-1} and so on. The “hard-sphere collision rate detailed balance” approach used above is a crude way of doing this, the master equation / ILT and capture rate approaches already used by the authors for the subsequent steps are more advanced alternatives (that should lead to rate coefficients with similar orders of magnitude). Or in other words, the authors already have the tools needed to do the kinetic analysis correctly, they just need to apply them (and report all the key results) properly.

Reply: We thank the reviewer for this detailed analysis and valuable suggestion. We agree that (K_{eq}) is only valid under the assumption that ($k_{-1} \gg k_f[\text{H}_2\text{O}]$), which is not necessarily satisfied for the strongly bound CI-HONO complexes considered in this work. As pointed out by the reviewer, the reaction of the CI-HONO complex with H_2O dominates over its dissociation rate. Therefore, the equilibrium approximation is not appropriate for describing the kinetics of these systems. As recommended by the reviewer, we have revised our kinetic calculations using the steady-state approximation (SSA), in which the equilibrium constant term is replaced by $(k_1/(k_{-1}+k_f[\text{H}_2\text{O}]))$. The required rate coefficients, (k_1), (k_{-1}), and (k_f), were explicitly estimated. In the revised manuscript, we have updated the

kinetic calculations accordingly. Additional details of the rate calculations are provided in Section 2 of the ESI.

Comment: On page 8, lines 237-238, the authors mention that the CI + SO₂ reactions were not included in the branching ratio calculations due to the lack of available data. Further, they mention that inclusion of the CI + SO₂ reactions did not affect the branching fraction calculations. Do the authors mean the lack of data regarding atmospheric concentration of SO₂, or available reaction rate constants? I feel this needs to be clarified a bit. I also think that the numbers including SO₂, if these were calculated, could be included in the SI to show that including SO₂ made a minimal difference.

Reply: We have not included the CI + SO₂ reactions in the branching ratio calculations due to the sparse availability of reaction rate constant data over the temperature range considered in the present study. In the revised manuscript, we have clearly mentioned this. We have now included the effective rate constant values for CI + SO₂ reactions in the branching fraction calculation at available temperatures (Table S15–S18 of ESI). It is evident from Tables S15–S18 of ESI that in the branching ratio calculation, inclusion of the SO₂ has a negligible effect on the calculated branching fractions.

Comment: Are the energies in Figures 1-4 zero-point vibrationally corrected electronic energies? It would be useful to add this detail to the figure captions.

Reply: In the revised manuscript, in the figure captions, we have mentioned that all relative energies shown are zero-point vibrationally corrected electronic energies.

Comment: Technical comments (corrections in bold):

1)Page 1, line 19: “Among various oxidizing agents, the OH radical is...”

2)P. 2, l. 36: “... bimolecular reactions of stabilized Criegee intermediates (sCIs) lead...”

3)P. 2, l. 41: “Water vapor is one of the most abundant greenhouse gases in...”

4)P. 2, l. 49-51: “Since the title reaction is a hydrogen atom transfer (HAT) reaction, we believe the study of CI + HONO and its real impact in the atmosphere is incomplete without investigating the role of water on the mechanism and kinetics.”

- 5) P. 3, l. 78: "As shown above, the reaction is a four steps reaction."
- 6) P. 3, l. 83: "For this kind of reaction, if one assumes an equilibrium for the first step, the overall termolecular rate..."
- 7) P. 3, l. 88: "THERMO uses the following equation..."
- 8) P. 4, l. 107: "The energetics and kinetics of the..."
- 9) P. 4, l. 109-110: "For completeness and comparison, we are summarizing here the results of our previous study." Only one study is cited, are there others as well? If so, they should also be cited.
- 10) P. 4, l. 110: "The study showed that the uncatalyzed reaction with HONO proceeds via hydrogen atom transfer (HAT) path."
- 11) P. 4, l. 113: "... addition, in our previous work, we have also..."
- 12) P. 5, l. 119: "The computed potential energy surfaces (PESs) for..."
- 13) P. 5, l. 122-124: "For all four reactions, in Path-A, first the CIs and HONO combine to form bimolecular complexes, namely CH₂OO–HONO, (CH₃)₂COO–HONO, anti-CH₃CHOO–HONO, and syn- CH₃CHOO–HONO, with stabilization energies (with respect to isolated reactants) of -10.14 kcal mol⁻¹,..."
- 14) P. 5, l. 125: "It is important to note that the CI-HONO bimolecular complex is also..."
- 15) P. 5, l. 126: "In Path-B, the HONO–WM (stabilizing energy of -5.79 kcal mol⁻¹) complex..."
- 16) P. 5, l. 126-128: "In Path-C, the CIs react with a WM to form bimolecular complexes, i.e. CH₂OO– WM, (CH₃)₂COO–WM, anti-CH₃CHOO–WM, and syn-CH₃CHOO–WM, with stabilization energies of - 6.78 kcal mol⁻¹,..."
- 17) P. 5, l. 129-130: "In all four cases, in the second step, these bimolecular complexes react with the remaining third species to form termolecular reactive complexes, namely RC1, RC2, RCanti, and RCsyn, with stabilization energies of -17.93 kcal mol⁻¹,..."
- 18) P. 5, l. 133: "... with stabilization energies of..."
- 19) P. 5, l. 135: "... covalent O–H bond between the terminal O-atom in the CIs and H-atom in HONO."
- 20) P. 5, l. 135: "The effective energy barriers of the TSs..."
- 21) P. 5, l. 137: "In the last step, the PCs dissociate to form..."
- 22) P. 5, l. 140: "... barrier of the catalyzed paths compared to the..."
- 23) P. 5, l. 141: "... for the WM catalyzed paths lie..."
- 24) P. 5, l. 145: "... in the WM catalyzed paths are..."
- 25) P. 5, l. 146-147: "... respectively, compared to the corresponding uncatalyzed paths."
- 26) P. 5, l. 149: "Therefore, to assess..."
- 27) P. 6, l. 153: "in the temperature range of..."
- 28) P. 6, l. 176-177: "The effective rate constants of the catalyzed reactions are tabulated in Tables 1-4 in temperature range of 213–320 K, along with the same for the uncatalyzed reactions."

- 29) P. 6, l. 179: "... that in the whole temperature range the uncatalyzed effective..."
- 30) P. 6, l. 180: "Even at high humidity conditions (RH=100%) the uncatalyzed effective rate..."
- 31) P. 6, l. 181: "... i.e. keff for the uncatalyzed reaction..."
- 32) P. 6, l. 182: "For example, at 298 K, keff for the catalyzed paths at..."
- 33) P. 6, l. 183-184: "while the same for the uncatalyzed is 6.41×10^1 s⁻¹. In contrast, for the remaining three WM catalyzed reactions,..."
- 34) P. 7, l. 185: "... catalyzed reactions dominate over the..."
- 35) P. 7, l. 186-187: "For the WM catalyzed (CH₃)₂COO + HONO reaction, (Table 2) in the whole temperature range the catalyzed path dominates over the uncatalyzed path at both low and high humidity conditions."
- 36) P. 7, l. 187: "At high humidity (RH=100%) the catalyzed path is"
- 37) P. 7, l. 188: "Even at low humidity (RH=20%) the catalyzed path dominates over"
- 38) P. 7, l. 189: "... for the catalyzed path at RH=20%..."
- 39) P. 7, l. 191: "... the dominance of the catalyzed path increases..."
- 40) P. 7, l. 194: "Similarly, for the WM catalyzed anti-CH₃CHOO + HONO,..."
- 41) P. 7, l. 211: "Similarly, we have compared the remaining three WM catalyzed..."
- 42) P. 7, l. 216: "... that the WM catalyzed reaction also dominant..."
- 43) P. 8, l. 218: "... magnitude slower than the WM catalyzed..."
- 44) P. 8, l. 219: "It clearly indicates that, in presence of water, the (CH₃)₂COO + HONO..."

Furthermore, I encourage the authors to carefully review the manuscript for text flow, especially Sections 2 and 3.

Reply: Thanks to the reviewer for the suggestions, the mentioned technical corrections have been incorporated in the revised manuscript. In addition, we have carefully proofread the whole manuscript and tried to remove all such mistakes