

Response to the Reviewer’s Comments

July 4, 2026

1 REFEREE REPORT

Comment: First, the construction of the rate coefficients for these reactions as a quasi-equilibrium for the three possible pairwise complexes followed by a reaction of that complex with the third species makes some assumptions about the kinetics of the initial complex that may not be realized. Take for example, the initial complex of the Criegee intermediate with HONO (path A). One common fate of that complex is to simply proceed to products; the uncatalyzed reaction is relatively facile, so it need not wait around for a water molecule. How do the authors treat that competition? It is surprising to me that the enhancement factors are so large (factor of 10), when other water enhancement factors in the atmosphere are smaller and then only when the uncatalyzed reaction is slower than the reactions with HONO are. The third-order rate coefficients are several orders of magnitude larger than for reactions of Criegee intermediates with water and NH_3 or with water dimer (e.g., *J. Phys. Chem* 2019, 123, 39, 8336–8348). Relatedly, I don’t completely understand the k_{eff} values as they end up being really large compared to collisional rates. Because the rate coefficients are so unusually large I would like to see more context for these calculated rate coefficients relative to other Criegee reactions and to collision rates, with discussion of the physical reasons for why they differ.

Reply: We agree with the reviewer that the enhancement factor appears to be large. We have used the equilibrium approach ($K_{eq} = k_1/k_{-1}$) to calculate the formation of the bimolecular complexes, which is overestimating the rate coefficients. Therefore, in the revised manuscript, we have replaced the pre-equilibrium approximation with a steady-state approximation (SSA), where $k_{SSA} = k_1/(k_{-1} + k_f[\text{H}_2\text{O}])$. In this approach, we explicitly calculate the bimolecular complex formation rate (k_1) and the back dissociation rate (k_{-1}) to the reactants. For the subsequent reaction of the

bimolecular complex with water, we calculate the collision rate ($k_f[\text{H}_2\text{O}]$). In the case of Path-A, the further collision rate with water is higher than the dissociation rate of the complex. For example, for Path-A WM catalyzed $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction at 298 K, dissociation rate (k_{-1}), and collision rate ($k_f[\text{H}_2\text{O}]$) are $4.45 \times 10^6 \text{ s}^{-1}$, and $1.39 \times 10^8 \text{ s}^{-1}$, respectively. Therefore, use of SSA approximation for the rate calculations is more appropriate. Using the SSA approximation, the calculated k_{eff} values become physically reasonable and remain below the collision limit.

The concern about larger third-order rate coefficients obtained for the WM-catalyzed $\text{CI} + \text{HONO}$ reaction can be attributed to the much stronger stabilization of the catalytic transition state compared with Criegee intermediate reactions with NH_3 , H_2O and $(\text{H}_2\text{O})_2$. For anti- $\text{CH}_3\text{CHOO} + \text{NH}_3 + \text{H}_2\text{O}$ reaction, the H_2O -catalyzed and NH_3 -catalyzed transition states were reported to be stabilized by -12.22 and $-7.36 \text{ kcal mol}^{-1}$, respectively. In contrast, for the anti- $\text{CH}_3\text{CHOO} + \text{HONO} + \text{H}_2\text{O}$ reaction investigated in the present work, the corresponding H_2O -catalyzed transition state is stabilized by $-19.51 \text{ kcal mol}^{-1}$, which is $\sim 7 \text{ kcal mol}^{-1}$ lower in energy than that of the $\text{NH}_3 + \text{H}_2\text{O}$ reaction. This greater transition-state stabilization, leading to larger third-order rate coefficients.

Regarding the other concern about the competition between the uncatalyzed and WM catalyzed reactions, as well as other competing reactions, we have calculated the branching fractions and explicitly included these competing reactions in the analysis. The results show that the contribution of the WM catalyzed reaction is significant under certain atmospheric conditions. For example, at the lowest temperature (213 K), the branching fractions of the WM catalyzed reaction for syn- CH_3CHOO and $(\text{CH}_3)_2\text{COO}$ are $\sim 80\%$ and 50% , respectively.

Comment: Second, the discussion of the branching is confusing (line 239). Under some conditions, other processes (like unimolecular decomposition) definitely contribute (fig 5), so why not list those in the equation? Also, Figure 5, where the catalyzed reaction with HONO is the third largest k_{eff} at the highest temperature for acetone oxide, is hard to reconcile with the statement “, for $(\text{CH}_3)_2\text{COO}$, the WM catalyzed reaction with HONO becomes the dominant atmospheric sink over the entire temperature range (213–320K) under both low and high humidity conditions” (lines 308-310). Also, describing this catalyzed reaction as dominant by 6 or 7 orders of magnitude, which the authors do in many places, seems at best to be true only in a narrowly defined set of conditions. I would welcome some clarification.

Reply: As suggested by the reviewer, we have revised the branching

fraction calculations to explicitly include the contribution from unimolecular decomposition. The corresponding equations and discussion have been updated in the revised manuscript to provide a more complete description of the contribution of the title reaction in the atmosphere. In the revised manuscript, we have clarified the relevant statements and explicitly specified the atmospheric conditions under which the WM catalyzed HONO reaction becomes a dominant sink. We have also revised the manuscript to avoid overstatements.

Furthermore, statements about the HONO reaction being dominant by several orders of magnitude have been revised to clearly specify the conditions under which this dominance occurs. This avoids overstatements and improves consistency between the discussion and the reported results.

Comment: Third, is there any reason to think other water catalyzed reactions could be similarly large? What is special about HONO above other trace species? Could future investigations of other reactions be expected to potentially change the authors' conclusions about dominance of this reaction?

Reply: WM catalyzed reactions involving other atmospheric species may also contribute to Criegee intermediate removal if they proceed through similarly efficient catalytic mechanisms. As discussed in Comment 1, the large rate coefficients for the WM-catalyzed CI + HONO reaction arise from the greater stabilization of the catalyzed transition state. Therefore, if other WM-catalyzed reactions exhibit a comparable transition-state stabilization, they could also possess similarly large rate coefficients. The atmospheric importance of a reaction is determined not only by its rate coefficient but also by the atmospheric concentration of the reactants. HONO is of particular interest because it is present at high concentrations in the atmosphere and can efficiently react with Criegee intermediates through a hydrogen atom transfer mechanism that is strongly enhanced by water catalysis. Nevertheless, if another atmospheric species were found to react with Criegee intermediates through a similarly efficient WM catalyzed mechanism and were present at concentrations comparable to or higher than HONO, its contribution could become significant and potentially alter the relative importance of the HONO reaction.