This review was conducted by a co-review team.

In the manuscript titled "How humidity makes HONO the dominant sink of alkyl substituted Criegee intermediates and a key nocturnal source of OH radicals", the authors investigate the reaction of several Criegee intermediates (CIs) with HONO, catalyzed by a water molecule. Using *ab initio* methods, the authors calculate reaction rate coefficients for the CI + HONO + H_2O reactions and incorporate these into the GEOS-Chem transport model. Indeed, by including these reactions they find that the reactions studied are major sinks of CIs and sources of OH radicals in the atmosphere.

Scientific significance: 4

Scientific quality: 3

Presentation quality: 3

I do not have the expertise to review the atmospheric modeling part of the manuscript, but the authors' approach seems reasonable. The *ab initio* methods used also appear to be standard and reasonable. The topic is also highly relevant and interesting. However, there are still some issues that the authors need to address before I can recommend the manuscript for publication.

1) 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.
2) Please add citations on page 3, line 63, to both the method and basis set used.
3) 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.
4) I wonder how realistic it is to use [HONO] = 8.8E10 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?
5) 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 3E-10 cm^3 s^{-1}. Using the same [HONO] value as the authors used, [HONO] = 8.8E10 cm^{-3}, the maximal k_{eff} becomes 3E-10 cm^3 s^{-1} * 8.8E10 cm^{-3} = 26.4 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.
6) Closely related to the problem described above is the equation on page 3, line 85. This equation only holds when $k_{-1} >> k_f$, 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 $k_{diss} = k_{coll} * p_{ref} * \exp[(-dG)/(RT)]$. Then assuming k_{coll} = 3E-10 cm^3 s^{-1}, p_{ref} = 1 atm = 2.5E19 cm^{-3}, T = 298 K, and using the dG value for $(CH_3)_2COO$-HONO (-2.88 kcal/mol, from Figure S2), $k_{diss} \approx$ 5E6 s^{-1}. This process competes with $k_{coll} * [H_2O]$. Assuming a relative humidity of 100%, at 298 K $[H_2O] \approx$ 7E17 cm^{-3}, and thereby $k_{coll} * [H_2O] \approx$ 2E8 s^{-1}. So ultimately it is

40 times more likely that the $(CH_3)_2COO$-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.

7) On page 8, lines 237-238, the authors mention that the CI + SO_2 reactions were not included in the branching ratio calculations due to the lack of available data. Further, they mention that inclusion of the CI + SO_2 reactions did not affect the branching fraction calculations. Do the authors mean the lack of data regarding atmospheric concentration of SO_2, or available reaction rate constants? I feel this needs to be clarified a bit. I also think that the numbers including SO_2, if these were calculated, could be included in the SI to show that including SO_2 made a minimal difference.
8) 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.

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 intermediate**s** (sCI**s**) 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 **k**inetics 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 CH_2OO–HONO, $(CH_3)_2COO$–HONO, anti-CH_3CHOO–HONO, and syn-CH_3CHOO–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. CH_2OO–WM, $(CH_3)_2COO$–WM, anti-CH_3CHOO–WM, and syn-CH_3CHOO–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, RC_{anti}, and RC_{syn}, 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. k_{eff} for **the** uncatalyzed reaction…”
32) P. 6, l. 182: “For example, at 298 K, k_{eff} **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 $(CH_3)_2COO$ + 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-CH_3CHOO + 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** $(CH_3)_2COO$ + HONO…”

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