**Atmospheric
Chemistry
and Physics
Discussions**

# Interactive comment on "Thermodynamics of reactions of ClHg and BrHg radicals with atmospherically abundant free radicals" *by* T. S. Dibble et al.

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Reply to referee report by K. A. Peterson

1) The present article is a very good survey of the reactivity/stability of HgX species with a variety of atmospheric radicals. The calculations are accurate enough for the purposes of this study and there is sufficient comparison to higher level ab initio results.

Reply: We appreciate Dr. Peterson's kind words.

2) My only major concern is in regards to the first part of Sec. 3.2, which involves the reactivity of Hg with BrO and ClO. The author considers both the insertion, BrHgO,

and oxygen end-on, BrOHg, species. In particular the latter has only a van der Waals interaction, which matches our experience as well. However, I don't understand why the HgBrO and HgClO species are not considered as possible products of the Hg + XO reaction... This would seem to contradict some of the conclusions of the present work. Not seriously, but enough to warrant modifying a few statements in the abstract and conclusion sections.

Reply: We explicitly assumed in Section 3.2, following Raofie and Ariya (2004), that the insertion reaction, Hg + BrO –> BrHgO, had a high barrier. Although our reasoning was not explained in the manuscript, we thought this to be consistent with the high barrier determined for Hg + Br2 –> BrHgBr (Balabanov, et al., 2005 in our ms). In preparing this response, we re-read that paper and noted a preliminary result for the barrier to Hg + BrO –> BrHgO: a barrier higher than that for Hg + Br2 –> BrHgBr! We will cite this result in the revised manuscript and make explicit the assumption that the barrier to Hg + ClO –> ClHgO is also too high for this reaction to be important in the atmosphere.

3) In Table I, I was surprised that there were not more previous results given for these halogen oxides and such. Certainly there must be previous CCSD(T) results for many of these fundamental species.

Reply: The approach used in the single theoretical result we cited in Table 1 included four (4) refinements that are not commonly seen in calculations on mercury, each of which might alter bond energies by 1-3 kcal/mol: (1) calculation of structures at CCSD(T); (2) extrapolation of CCSD(T) energies to the basis set limit; (3) accounting for relativistic effects; and (4) accounting for residual core-valence correlation.

We are not aware of any other work on HgBr2 or HgCl2 that includes even two of these four refinements. We regard the work cited in the Table as the most accurate and reliable, by far, of all previous studies on these two compounds. As our goal was to validate our computational approach, we cited only that theoretical work that we regarded as a valid benchmark.

4) In Table 3 it would be useful to know what the connectivity is for these molecules. In the caption, shouldn't a negative bond energy refer to favorable dissociation to X+Hg rather than dissociation to atoms as currently stated since these are bond enthalpies?

Reply: We will clarify the connectivity. We thank the referee for catching the error in the Table caption, and will change "atoms" to "X + Hg".

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 17887, 2012.

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