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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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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.

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. Both of these resulting radicals (both with doublet-Pi ground states) were predicted in the work of Balabanov and Peterson (2003b in the present reference list) to be quite stable: 90.4 and 84.5 kJ/mol for the 0 K bond strengths of Hg-ClO and Hg-BrO, respectively. 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.

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.

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?

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