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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.

Anonymous Referee #3

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Recent studies indicate that HgBr may be the sole important intermediate in the oxidation of atmospheric elemental mercury under most atmospheric conditions. Since HgBr is not strongly bound and may decompose reversibly, the knowledge of its forward reactions is crucial for evaluating the overall rate of atmospheric mercury oxidation. While there exist several experimental and theoretical investigations of the HgBr formation, subsequent fate of this radical-intermediate is poorly known. To address this deficiency, Dibble et al. have conducted quantum chemical calculations to investigate the thermodynamic feasibility of several chemical pathways involving HgCl and HgBr radical intermediates with selected abundant atmospheric radicals. Additionally, the thermochemistry of the reaction between elemental mercury and BrO/ClO radicals to

form HgOBr/HgOCl and the electron affinities of selected mercury products (to facilitate their detection by chemical ionization mass spectrometry) are also evaluated.

The calculations have been conducted at an appropriate level of theory. Where data exist, there is a good agreement with previous experimental and/or theoretical results. The conclusions of this study are well justified and will be of significant interest to the atmospheric science community involved in atmospheric mercury research, including both experimentalists and modelers. From my viewpoint, the significant quality of this manuscript, making it worthy of publication, is that it highlights the issue that the knowledge of the secondary chemistry of mercury oxidation intermediates is crucial in evaluating the overall atmospheric mercury depletion. I recommend the manuscript to be published as is.

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