

# Theoretical kinetics of reactions of •HgBr critical to oxidation of atmospheric mercury

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## Abstract text

Atomic bromine (Br) is known to initiate oxidation of gaseous elemental mercury, Hg(0), in the marine boundary layer and in polar mercury depletion events. Br is also suggested to be the primary global oxidant of Hg(0). This process is initiated via the reaction  $\text{Hg} + \text{Br}\bullet + \text{M} \rightarrow \text{BrHg}\bullet + \text{M}$ . The second step is suspected to be reaction of BrHg• radical with atmospherically abundant radicals, Y•, to form stable compounds: BrHgY. Unfortunately, rate constants for reactions of BrHg• have never been measured, and there has yet to be any experimental detection of these BrHgY species, even in the laboratory.

We used computational chemistry to characterize these species and determine the rate constants for BrHg reaction with the two most abundant Y (NO<sub>2</sub> and HOO). Coupled cluster theory and multireference perturbation theory are employed to investigate the potential energy for bond formation, and high-pressure limiting rate constants are computed by variational transition state theory for 200 K ≤ T ≤ 400K. The basis set, denoted as AVTZ, was constructed from small-core relativistic effective core potentials and valence aug-cc-pVTZ basis set. Using CASPT2/AVTZ//PBE0/AVTZ, computed rate constants for BrHg• + NO<sub>2</sub> and HOO are very high:  $2.3 \times 10^{-11} \text{ e}^{+401/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $8.6 \times 10^{-12} \text{ e}^{+750/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. We further estimated the combined pressure-temperature dependence of these rate constants using an RRKM/Master Equation approach. These results suggest that *syn*-BrHgONO and BrHgOOH should be two major oxidized mercury compounds formed in the gaseous atmosphere. A competing product channel to form Hg(0) + BrY is competitive in the case of Y=NO<sub>2</sub> but is of minor importance for Y=HOO.

Reactions of BrHg• with hydrocarbons appear to be of negligible importance due to the weakness of the BrHg-H bond and bonds between BrHg• and sp<sup>2</sup>-hybridized carbon atoms.