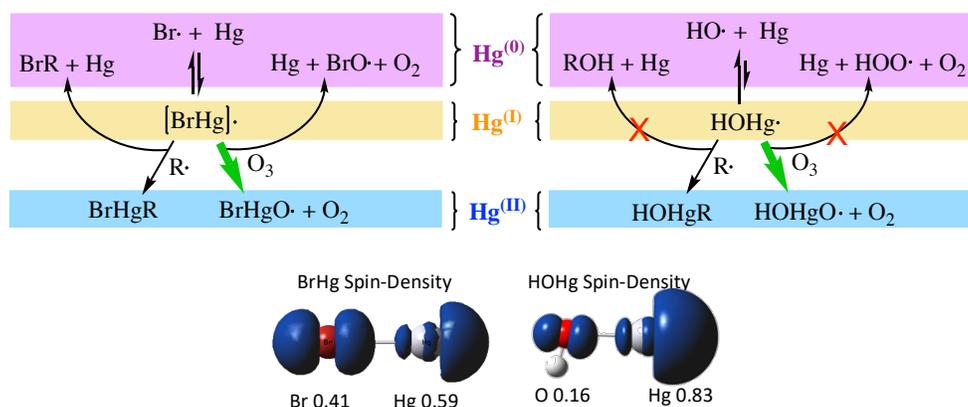


Ozone as an Oxidant and Reductant of Atmospheric Hg(I)

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Mercury is well-known as one of the most toxic metals for vertebrates, and it can be released to the environment from natural and artificial sources. Mercury's ability to travel through the atmosphere far from emission sources makes it an important global pollutant. Mercury emissions to the atmosphere mostly occur as gaseous elemental mercury ($\text{Hg}^{(0)}$), but mercury deposits to ecosystems most easily as $\text{Hg}^{(\text{II})}$ compounds rather than $\text{Hg}^{(0)}$. Therefore, it is crucial to understand the facile interchange of mercury between elemental $\text{Hg}^{(0)}$, monovalent $\text{Hg}^{(\text{I})}$ and divalent $\text{Hg}^{(\text{II})}$ forms to understand biogeochemical cycling of mercury.



Abundant evidence exists that $\text{Br}\cdot$ can initiate the oxidation of $\text{Hg}^{(0)}$, leading to $\text{Hg}^{(\text{I})}$ in the form of $\text{BrHg}\cdot$. According to the linearized density from the Orbital-Optimized Coupled-Cluster Doubles (OOCCD) method, this species of $\text{Hg}^{(\text{I})}$ is characterized by an almost equally distributed spin-density on Br and Hg. Therefore, depending on the orientation of molecular collisions with radicals, it can form $\text{Hg}^{(\text{II})}$ or $\text{Hg}^{(0)}$. On the other hand, it is believed that $\text{HO}\cdot$ can mimic $\text{Br}\cdot$ to analogously produce $\text{HOHg}\cdot$. This radical owns the unpaired electron mostly on Hg, which impose a high barrier for reduction reaction. Therefore, unlike $\text{BrHg}\cdot$, $\text{HOHg}\cdot$ preferentially lead to $\text{Hg}^{(\text{II})}$ species but not to $\text{Hg}^{(0)}$. This work has been focused in the kinetic properties of the oxidation and reduction reactions of YHg ($\text{Y} = \text{Br}$ or HO) with O_3 , by means of a combination of state-of-the-art quantum chemistry methods such as CAM-B3LYP-D3BJ, MRCI+Q, NEVPT2, AQMRCC, CR-CC(2,3) and CCSD(T), in combination with aug-cc-pVTZ-PP and Stuttgart-Koln small-core multiconfiguration-Dirac-Hartree-Fock-adjusted (SK-MCDHF-RSC) effective core potentials for Br and Hg, and aug-cc-pVTZ for oxygen and hydrogen atoms.

We show that independently of the nature of Y (Br or HO), the $\text{YHg}\cdot$ compounds seems to be barrierless oxidized by ozone, opening an efficient reaction pathway toward $\text{Hg}^{(\text{II})}$ species. It seems likely that $\text{HOHg}\cdot + \text{O}_3$ has a higher rate than the dissociation of HOHg , thus, OH could be effective in oxidizing $\text{Hg}^{(0)}$ to $\text{Hg}^{(\text{II})}$. This finding may resolve a long-standing dispute in the literature between physical chemistry arguments against ozone or OH as effective oxidants of $\text{Hg}^{(0)}$ and field data in the continental boundary layer that is hard to explain using Br to initiate oxidation.