Toward Identifying Mercury(II) Compounds in the Atmosphere

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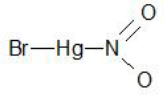
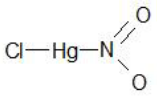
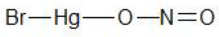
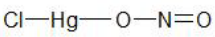
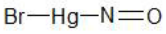
Atmospheric compounds containing mercury have long been of concern, due to the fact that mercury has a long atmospheric residence time and high toxicity. In the atmosphere, gas phase elemental mercury ($Hg_{(g)}$) is oxidized to Hg(II) compounds, but these Hg(II) compounds remain unidentified. Field experiments suggest that oxidation is initiated by reactions with atomic bromine and, to a lesser extent, atomic chlorine. We hypothesized that the XHg• compounds for (X = Cl, Br) formed in these reactions, react with the more abundant atmospheric radicals to form stable XHgY compounds. The abundant radicals include NO, NO_2, and HOO; reaction with O_2 to form peroxy radicals is also possible. The potential XHgY compounds that represent atmospheric Hg(II) compounds are shown below.

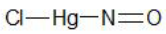


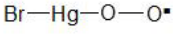


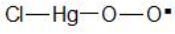


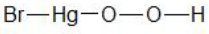


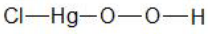












Quantum calculations used density functional theory (B3LYP), starting with the modest LANL2DZ basis set for optimizing geometries and computing harmonic vibrational frequencies. These calculations were then repeated with a much larger aug-cc-pVTZ basis set on all atoms, with an effective core potential basis set (ECP60MDF) to explicitly account for the relativistic effects of the core electrons of mercury. From these calculations we report the bond energies, ionization energies, electron affinities, and proton affinities for each compound. Most importantly, calculations show that three sets of compounds:

$XHgNO_2$ XHgONO XHgOOH

are thermally stable, and could be key contributors to the Hg(II) compounds. Studies of the ions indicate that while the electron affinities of Hg(II) compounds are quite low (~2.05-3.15 eV), and ionization energies are high (~8.30-10.40 eV), proton affinities are in a moderate range (~6.20-7.25 eV) indicating that the compounds could be isolated via chemical ionization mass spectroscopy.