Thermodynamics limits the reactivity of BrHg• radical with volatile organic compounds

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Abstract

Mercury emissions to the atmosphere primarily consist of Hg(0), which tends not to enter ecosystems until it is oxidized. Atomic bromine initiates oxidation of Hg(0) via the BrHg• intermediate, but the further reactions of BrHg• are just beginning to be explored. Here we use quantum chemistry to determine that hydrogen abstraction from hydrocarbons by BrHg• is so endothermic as to be irrelevant. Bonds between BrHg• and carbon atoms are so weak that BrHg• addition to carbon-carbon double bonds atoms will be somewhat ineffective in leading to further reactions.

Keywords: atmospheric chemistry, reactive gaseous mercury, kinetics, radicals

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1. Introduction

Mercury is a neurotoxin. The atmosphere acts as a highway to transport mercury around the globe.^{1, 2} Mercury is emitted to the atmosphere primarily as gaseous elemental mercury (Hg(0)).³ Due to its relatively high equilibrium vapor pressure and low water solubility, gaseous Hg(0) is only very slowly deposited to the Earth's surface.¹ By contrast, gaseous oxidized mercury (GOM) compounds have much lower vapor pressures and higher water solubility, and are much more efficiently transferred from the atmosphere to soil and water. Upon entering ecosystems, oxidized mercury can be transformed into organomercury compounds, which bioaccumulate as one rises up the food chain.⁴ Sensitivity studies show that our ignorance of the kinetics and mechanism of mercury oxidation create enormous uncertainties in the geographic distribution of mercury deposition.⁵ This ignorance also creates large uncertainties in the atmospheric lifetime of mercury, which hinders efforts to understand its transport and cycling between the atmosphere, hydrosphere, lithosphere, and biosphere.⁵

Recent field and modeling studies have focused on the role of atomic bromine (Br) in initiating Hg(0) oxidation in the atmosphere.^{6, 7} This process is initiated by the reaction:^{8, 9}

where M is a third body. Unfortunately, the subsequent chemistry has scarcely been studied. Goodsite et al considered the reaction of BrHg• with OH and Br, finding both HgBr₂ and BrHgOH to be stable gas-phase compounds.⁸ They also estimated the rate constant for HgBr₂ formation:

at 1 atmosphere total pressure, while Balabanov et al. computed the rate constants for various product channels of the $\text{BrHg}\cdot + \text{Br}$ reaction.¹⁰ The rate constant of reaction (2) is about $1/10^{\text{th}}$ of the collision limit, due to the fact that the reaction is the barrierless addition of two radicals.^{8, 10} Atmospheric models can account for the global oxidation of mercury while invoking reaction (1) as the sole process as initiating $\text{Hg}(0)$ oxidation.^{11, 12} Theoretical work in our group suggested the existence of other barrierless addition pathways, namely the reaction of $\text{BrHg}\cdot$ with a variety of atmospherically abundant radicals, Y ($\text{Y}=\text{NO}_2$, HOO , ClO , BrO , and IO).^{13, 14} This suggestion has been widely accepted, but the reaction of $\text{BrHg}\cdot$ with other atmospheric trace gases, such as volatile organic compounds (VOCs), has yet to be considered.

This paper considers two classes of reactions, starting with hydrogen abstraction from VOCs:

We present results for the dissociation energy of the BrHg-H bond that clearly indicate that $\text{BrHg}\cdot$ cannot abstract hydrogen atoms from VOCs at atmospheric temperatures. The second class of reactions is addition of the $\text{BrHg}\cdot$ radical to sp^2 -hybridized carbon atoms, using ethylene and benzene as models for the classes of olefinic and aromatic hydrocarbons:

We find that the BrHg-C bond energy is so weak as to prevent the addition of $\text{BrHg}\cdot$ to aromatic hydrocarbons and limit the importance of $\text{BrHg}\cdot$ addition to alkenes.

2. Computational Methods

Calculations were carried out using Revision D01 of the Gaussian09 program.¹⁵ The small-core Stuttgart/Cologne scalar relativistic pseudopotentials for Br (10 electrons) and Hg (60 electrons) were used in conjunction with the corresponding aug-cc-pVTZ basis sets for the electrons treated explicitly.^{16, 17, 18} The standard Dunning correlation consistent basis sets aug-cc-pVTZ were used for hydrogen and carbon atoms.^{19, 20} This combination of basis sets is referred to here as AVTZ. Radicals were treated with the spin-unrestricted formalism. Structures and harmonic vibrational frequencies of reactants, products, and transition states (more commonly, but inaccurately, called transition states) were determined with the PBE0²¹ and M06-2X²² functionals, both of which demonstrated very good performance for the structures, vibrational frequencies, and thermodynamics of other mercury compounds when used with the AVTZ basis set.^{14, 23} PBE0 and M06-2X calculations reported here used a pruned grid of 99 radial shells with 590 angular points per shell, which is finer than the default grid. Reactants and products were verified to be potential energy minima. The identity of transition states was checked by examining the nature of their single imaginary frequencies. Energies were refined using the coupled cluster single, double, and non-iterative triple excitations (CCSD(T)) method.^{24, 25} For a limited set of species, geometries and vibrational frequencies were also obtained using CCSD. For the same species, CCSD(T) energies were also calculated using the corresponding AVQZ basis set. CCSD and CCSD(T) calculations used the frozen core approximation. The range of molecular orbitals to be correlated was set as the 5d and 6s electrons of Hg, the 4s and 4p electrons of Br, the 1s electrons of H, and the 2s and 2p electrons of C.

Relative energies reported herein are at 0 K and include zero-point energies, and so are equivalent to enthalpy changes at zero K. Gibbs Free Energy changes were computed as a function of temperature. Computations of zero-point energies and Gibbs Free Energies used the rigid rotor and harmonic oscillator approximations without any scaling of vibrational frequencies. Standard transition state theory was used to compute rate constants for reaction (4) as a function of temperature, T , via:

$$k_{TST}(T) = L \frac{k_B T}{h} \exp(-\Delta G^\ddagger(T) / RT) \quad (6)$$

where L is the reaction path degeneracy, k_B and R are, respectively, Boltzmann's constant and the gas constant, h is Planck's constant, and $\Delta G^\ddagger(T)$ is the molar Gibbs free energy of activation.

3. Results and Discussion

We first consider the bond dissociation energy, D_o , of the BrHg-H bond using three work reactions. These work reactions are listed in Table 1 together with their computed enthalpies of reaction. All three reactions involve conversion of BrHgH into HgBr₂, as HgBr₂ is one of the few compounds with a BrHg substituent for which the ΔH_f° (0 K) is known. We use the theoretical ΔH_f° (0 K) value obtained by Balabanov and Peterson²⁶ (-16.3 kcal/mol) which is in good agreement with, but probably more reliable than, the experimental value (-16.1 ± 2.0 kcal/mol).²⁷ Fortunately, experiment provides very precise knowledge (± 0.04 kcal/mol) of D_o for •HgH,²⁸ and reasonable precision (± 0.6 kcal/mol) for D_o of BrHg•.²⁹ Values of ΔH_f° (0 K) for all species in Table 1 are listed in the Supplementary Material.^{30, 31} Note that all uncertainties quantified here refer to 95% confidence intervals (95% CI).

Table 2 lists the values of ΔH_f° (0 K) and D_0 for BrHg-H implied by the three work reactions. Work reactions B and C agree well with each other for the implied value of D_0 and exhibit much smaller variability in D_0 across theoretical methods than work reaction A. In addition, the value of D_0 obtained in work reaction C is converged with respect to basis set at the CCSD(T) level. As a result, we favor the values of 73.0-73.5 kcal/mol obtained by work reactions B and C. We estimate a 95% confidence interval (CI) in D_0 due to errors in the quantum calculations of ± 3 kcal/mol. Uncertainties in the literature values of ΔH_f° (0 K) for BrHgBr (see Table S2) are estimated to contribute 1 kcal/mol to the 95% CI. The resulting value of D_0 is 73 ± 3 kcal/mol.

C-H bonds in alkanes possess D_0 of ~ 100 kcal/mol.^{30, 31} C-H bond energies are larger when the carbon atom is sp^2 - or sp -hybridized, as in alkenes or aromatics and alkynes, respectively. These bond energies are much higher than that of BrHg-H, so it is clear that BrHg• will not abstract hydrogen atoms from hydrocarbons at temperatures relevant to atmospheric chemistry.

Let us consider functionalize VOCs with low C-H bond energies. Ordinary aldehydes have much smaller C-H bond energies than alkanes, 86.7 ± 0.2 kcal/mol for $CH_2=O$ and 87.9 ± 0.5 kcal/mol for $CH_3CH=O$.^{30, 31} These bond energies imply rate constants for hydrogen abstraction by BrHg• that are, at the very least, seven orders of magnitude lower than the collision limit. α,β unsaturated carbonyl compounds such as glyoxal ($O=CHCH=O$) and acrolein ($CH_2=CHCH=O$) do not possess C-H bond energies lower than that of $CH_2=O$.³² The CH_3OO-H bond energy of 84.3 ± 0.3 kcal/mol (smaller by 1.9 kcal/mol than that for $HOO-H$)^{30, 31} still implies a rate constant for BrHg• abstracting hydrogen from ROOH compounds that is at least 6 orders of magnitude slower than the collision limit. Note that the thermodynamic arguments above do not

take into account any barrier above the enthalpy of reaction. As noted above, the currently expected fate of BrHg• in the atmosphere is barrierless addition to radicals (primarily NO₂ and HOO). The rate constants for these reactions are expected to be roughly 1/10th of the collision limit: $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.^{13, 33} As concentrations of aldehydes and ROOH rarely exceed that of NO₂ by even three orders of magnitude in the daytime atmosphere, we can conclude that hydrogen abstraction from VOCs by BrHg• will not be important to the atmospheric fate of BrHg•.

Another common reaction for atmospheric radicals is addition to sp²-hybridized carbon atoms in alkenes and aromatic compounds. To explore this possibility, we examined the addition of BrHg• to ethylene, which is the prototype for alkenes:

We also considered the displacement reaction:

The analogous reactions were also investigated for benzene, which is the prototype for aromatic hydrocarbons. In the case of benzene, attempts to optimize the geometry of a covalently bound BrHgC₆H₆ radical (such as shown in Eqn. 5) were unsuccessful at both PBE0/AVTZ and M06-2X/AVTZ; the structure fell apart to the van der Waals complex. We also tried to optimize a BrHgC₆H₆ radical with the analogous double-zeta basis set and the older LANL2DZ basis set, but were unsuccessful. We conclude that such a covalently bound structure is absolutely unstable.

Figure 1 displays the structures of the reactants and products of reactions of BrHg with ethylene, as well as the structure of the transition state for reaction (7). We also find van der Waals complexes of BrHg• with ethylene and benzene. Such complexes are often found in radical addition to double bonds.^{34, 35} Figure 2 depicts the structures of this van der Waals complex along with that of the closed-shell BrHgC₆H₅ molecule. The PBE0 and M06-2X structures of these species agree well except in the case of the transition state for BrHgCH₂CH₂• formation. The structure of this TS is much later (more like products) at M06-2X than at PBE0. As we shall see below, this has little effect on the predicted activation barrier.

Table 3 lists the relative energies for BrHg• reacting with ethylene and benzene. We first briefly discuss displacement reaction (8) and the analogous reaction of BrHg• with benzene:

Both reactions are endothermic by roughly 40 kcal/mol, and, therefore, will not occur. The strength of the Hg-C bond in these molecules can be computed by subtracting ΔH_r° for reactions (8) and (9) from the known values of D_0 for the H-CH=CH₂ and C₆H₅-H bonds (109.0 and 111.3 kcal/mol, respectively).^{30, 31} The resulting strength of the Hg-C bond is roughly 63 kcal/mol at CCSD(T)/AVTZ (stronger by 1-8 kcal/mol using DFT). The strength of the π -bond of ethylene is about 63 kcal/mol,³⁶ implying that the addition of BrHg• to ethylene (reaction 7) will be essentially thermoneutral.

Inspection of Table 3 confirms the extreme weakness of the BrHg-CH₂CH₂• bond, as the energy of reaction (7) is only -0.3 to -0.4 kcal/mol at CCSD(T). As a further check, we verified that these small reaction energies arise from the stable wavefunctions of the BrHgCH₂CH₂• radical.

The two DFT methods disagree as to whether this reaction is slightly exothermic or slightly endothermic.

The potential energy profile for BrHg• addition to ethylene is shown in Figure 3. The addition of BrHg• to ethylene first forms a van der Waals complex that is bound by 2.6 kcal/mole at the CCSD(T)//PBE0 level of theory. A transition state separates this complex from the BrHgCH₂CH₂• radical. The energy of the transition state relative to separated reactants spans the range -0.8 to +2.6 kcal/mol. The CCSD(T)//PBE0 and CCSD(T)//M06-2X values agree very well with each other at +0.8 and +1.0 kcal/mole despite the very different transition state geometries at PBE0 versus M06-2X.

Because of this difference in the predicted geometry of the TS, we re-computed the geometry using CCSD and the smaller VTZ analog of the AVTZ basis set that was used in other calculations on this system. The CCSD/VTZ geometry is intermediate between the PBE0/AVTZ and M06-2X/AVTZ geometries. The energy of the CCSD/VTZ structure at CCSD(T)/AVTZ is +1.1 kcal/mol above reactants, which is nearly identical to the values in Table 3. We are, therefore, confident that the variability in computed TS structure is not affecting the computed barrier height.

We computed rate constants for the formation and dissociation of BrHgCH₂CH₂• for $200 \leq T \leq 400$ K. This temperature range spans the lowest temperatures relevant to atmospheric chemistry of mercury oxidation by Br and the highest temperatures at which BrHg• might live long enough to enable kinetic studies of its bimolecular reactions. The reaction path degeneracy, L , is 4 for the forward reaction but 1 for the reverse reaction. The values of k_7 in Table 4 are two to three orders

of magnitude lower than the expected values of the rate constants, cited previously, for BrHg• reaction with NO₂ and HOO.

The values in Table 4 are only valid in the high-pressure limit. Rather than carry out an analysis of the pressure dependence of k₇, we will draw conclusions from a more conceptual analysis of the elementary reactions:

where BrHgCH₂CH₂•* indicates activated (internal excited) radicals. In this analysis, k₁₀ is the high-pressure limiting value of k₇. The value of k₋₇ listed in Table 3 is for dissociation of thermalized BrHgCH₂CH₂•, so k₋₁₀ (for dissociation of energized BrHgCH₂CH₂•) is at least as large as k₋₇. The pseudo-first order rate constant for collision of BrHgCH₂CH₂• with air molecules at 1 atm is ~5 × 10¹⁰ sec⁻¹. We can see that, at 1 atm, BrHgCH₂CH₂•* will fall apart via reaction -10 *at least* 30 to 200 times faster than it will undergo even a single de-activating collision. As a result, reaction 7 is far from the high pressure limit at 1 atm, so its importance would seem to be much smaller than indicated by the values in Table 4. As a result, we conclude that BrHgCH₂CH₂• will not react with ethylene in the atmosphere.

As ethylene is the prototype for alkenes, it is tempting to generalize our conclusion to larger alkenes. However, addition of BrHg• to larger alkenes can form secondary or tertiary alkyl radicals, which are expected be more stable than a primary radical like BrHgCH₂CH₂•. Also, BrHg• addition to conjugated dienes (e.g., isoprene) or α,β unsaturated carbonyls (e.g., methacrolein or methylvinylketone) could lead to resonance-stabilized radicals. The enhanced

stability of these radicals would make their dissociation much slower than that of $\text{BrHgCH}_2\text{CH}_2\bullet$, potentially further reaction along the common pathways for carbon-centered radicals.

4. Conclusions

The BrHg-H bond energy is sufficiently weak ($\sim 73 \pm 4$ kcal/mole) that the $\text{BrHg}\bullet$ radical cannot abstract hydrogen atoms from carbon atoms. This means that this large class of reactions common to radicals in the atmosphere is not feasible for BrHg . In addition, the BrHg-C bond is essentially as strong as the π bond in alkenes- roughly 63 kcal/mol. This means that BrHg-C bonds formed in $\text{BrHg}\bullet$ addition to C-C double bonds may tend to break before the resulting carbon-centered radical can undergo further reactions. As a result, $\text{BrHg}\bullet$ oxidation to Hg(II) by addition to sp^2 -hybridized carbon atoms might only occur to a limited extent. Further investigations of reactions of $\text{BrHg}\bullet$ with C_3 and larger alkenes are needed to fully assess the importance of this class of reactions for the atmospheric fate of $\text{BrHg}\bullet$.

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Supplementary Information

Absolute energies, zero-point energies, Cartesian coordinates, and vibrational frequencies of species in the reaction of $\text{BrHg}\cdot$ with ethylene and benzene; absolute energies, zero-point energies, and literature thermodynamics data for species involved in work reactions A-C.

Figure Captions

Figure 1. Structures of species involved in the reactions of BrHg• with ethylene. PBE0/AVTZ and M06-2X values (in square brackets) of bond lengths are in Ångstroms with valence angles and dihedral angles in degrees.

Figure 2. Structure of the van der Waals complex of BrHg• with benzene (two top views) and structure of the BrHgC₆H₅ molecule. PBE0/AVTZ and M06-2X values (in square brackets) of bond lengths are in Ångstroms with valence angles and dihedral angles in degrees. The C-C bond length in benzene is given for comparison.

Figure 3. Potential energy profile for addition of BrHg• to ethylene (kcal/mol at 0 K, including zero-point energy) using the AVTZ basis set. Thick lines illustrate the CCSD(T) relative energies computed with geometries and zero-point energies from PBE0. The thinner lines show the profile at PBE0 (with energies in italics), and the M06-2X energies are listed in square brackets.

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Graphical Abstract

Table 1. Enthalpies of work reactions (kcal/mol at 0 K, including zero-point energy) used to determine ΔH_f° (0 K) for (BrHgH) and D_0 for BrHg-H. The AVTZ basis set was used throughout, except where noted. CCSD(T) results use geometries and zero-point energies calculated at CCSD.

Work Reaction	M06-2X	PBE0	CCSD	CCSD(T)// CCSD
A) BrHgH + CH ₃ Br → BrHgBr + CH ₄	-34.2	-33.1	-29.3	-28.6
B) BrHgH + HBr → BrHgBr + H ₂	-17.7	-14.6	-13.6	-15.1
C) BrHgH + BrHg• → BrHgBr + •HgH	9.8	8.6	8.3	8.1 (8.1) ^a

a) Value in parentheses from CCSD(T)/AVQZ energies.

Table 2

Table 2. ΔH_f° for BrHgH and D_0 for BrHg-H (kcal/mol at 0 K) from various levels of theory using the AVTZ basis set, except where specified. CCSD(T) results use geometries and zero-point energies calculated at CCSD.

Work Reaction	M06-2X	PBE0	CCSD	CCSD(T)	CCSD(T)/AVQZ
	ΔH_f°				
A) BrHgH + CH ₃ Br → BrHgBr + CH ₄	7.0	5.9	1.8	1.4	--
B) BrHgH + HBr → BrHgBr + H ₂	8.1	5.0	5.0	5.5	--
C) BrHgH + BrHg• → BrHgBr + •HgH	4.2	5.5	5.7	5.9	5.9
	D_0				
A) BrHgH + CH ₃ Br → BrHgBr + CH ₄	72.0	73.1	77.2	77.6	--
B) BrHgH + HBr → BrHgBr + H ₂	70.9	74.0	74.0	73.5	--
C) BrHgH + BrHg• → BrHgBr + •HgH	74.8	73.5	73.2	73.0	73.0

Table 3

Table 3. Relative energies for reactions of BrHg• with ethylene and benzene (kcal/mol at 0 K, including zero-point energy) using the AVTZ basis set.

Reaction	PBE0	M06-2X	CCSD(T)// PBE0	CCSD(T)// M06-2X
BrHg• + CH ₂ =CH ₂ → BrHg•---CH ₂ =CH ₂	-1.5	-3.5	-2.6	--
BrHg• + CH ₂ =CH ₂ → BrHgCH ₂ CH ₂ •	-4.3	2.6	-0.4	-0.3
TS[BrHg• + CH ₂ =CH ₂ → BrHgCH ₂ CH ₂ •]	-0.8	2.8	0.8	1.0
BrHg• + CH ₂ =CH ₂ → H• + BrHgCH=CH ₂	38.0	42.7	45.8	--
BrHg• + C ₆ H ₆ → BrHg•---C ₆ H ₆	-2.2	-6.9	--	--
BrHg• + C ₆ H ₆ → H• + BrHgC ₆ H ₅	38.7	43.0	--	--

Table 4. Rate constants in the high-pressure limit for the reactions (7) and (-7) at CCSD(T)//PBE0/AVTZ.

Temperature (K)	k_7 (cm ³ molecule ⁻¹ sec ⁻¹)	k_{-7} (sec ⁻¹)
200	2.1×10^{-13}	1.5×10^{12}
250	4.0×10^{-13}	3.3×10^{12}
285	5.7×10^{-13}	4.9×10^{12}
333	8.6×10^{-13}	7.5×10^{12}
350	9.8×10^{-13}	8.4×10^{12}
400	1.4×10^{-12}	1.1×10^{13}

Figure 1

Figure 2

Figure 3