



Thermodynamics of reactions of ClHg and BrHg radicals with atmospherically abundant free radicals

T. S. Dibble, M. J. Zelig, and H. Mao

Chemistry Department, State University of New York-Environmental Science and Forestry, Syracuse, NY, USA

Correspondence to: T. S. Dibble (tsdibble@esf.edu)

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Abstract. Quantum calculations are used to determine the stability of reactive gaseous mercury (Hg(II)) compounds likely to be formed in the Br-initiated oxidation of gaseous elemental mercury (Hg(0)). Due to the absence of any evidence, current models neglect the possible reaction of BrHg with abundant radicals such as NO, NO₂, HO₂, ClO, or BrO. The present work demonstrates that BrHg forms stable compounds, BrHgY, with all of these radicals except NO. Additional calculations on the analogous ClHgY compounds reveal that the strength of the XHg–Y bond (for X = Cl, Br) varies little with the identity of the halogen. Calculations further suggest that HO₂ and NO₃ do not form strong bonds with Hg(0), and cannot initiate Hg(0) oxidation in the gas phase. The theoretical approach is validated by comparison to published data on HgX₂ compounds, both from experiment and highly refined quantum chemical calculations. Quantum calculations on the stability of the anions of XHgY are carried out in order to aid future laboratory studies aimed at molecular-level characterization of gaseous Hg(II) compounds. Spectroscopic data on BrHg is analyzed to determine the equilibrium constant for its formation, and BrHg is determined to be much less stable than previously estimated. An expression is presented for the rate constant for BrHg dissociation.

1 Introduction

The details of gaseous elemental mercury (Hg(0)) oxidation matter because wet and dry deposition of mercury is much more efficient for reactive gaseous mercury (Hg(II), RGM) than Hg(0) (Schroeder and Munthes, 1998). Deposition allows atmospheric mercury to enter ecosystems and,

ultimately, affect the health of humans and other animals. Sensitivity analyses show that the geographic distribution of mercury deposition is very sensitive to the assumed oxidation mechanism (Lin, et al., 2007; Seigneur et al., 2006).

The mechanisms of the oxidation of Hg(0) to Hg(II) are the subject of controversy (Subir 2011; Pirrone et al., 2008; Seigneur et al., 2006; Ariya et al., 2008). Until recently, hydroxyl radical (OH), ozone (O₃), hydroperoxide (H₂O₂), chlorine (Cl₂), and hydrochloride (HCl) were the major gas phase oxidants invoked in atmospheric models (Bollock et al. 2002; Petersen et al., 2001; Seignuer et al., 1994). The reported rate constant for reaction of O₃ with Hg(0) varies by a factor of ~20, and even by a factor of ~10 in the same laboratory (Hall, 1995; Pal and Ariya, 2004; Spicer et al., 2005; Sumner, et al., 2004). Calvert and Lindberg (2005) questioned the role of OH radical under atmospheric conditions. Atomic halogens (Br and Cl) have been invoked to explain the simultaneous decrease in concentrations of both O₃ and Hg(0) in mercury depletion events (Steffen et al. 2008, references therein; Obrist et al., 2011; Mao et al., 2011). Field data in the marine boundary layer has been analyzed to suggest a major role for Br in initiating Hg(0) oxidation (Sprovieri et al., 2010a), and recent models suggest that Br plays a dominant role in mercury cycling in the global troposphere (Holmes et al., 2009).

The rate constants for reaction of Cl and Br with Hg(0) in the gas phase have been measured as function of temperature and pressure by Donahoue et al. (2005, 2006). Their results reinforce the logical supposition that these X + Hg (X = Cl, Br) reactions are barrierless addition reactions:



Even before these rate constants were measured, Goodsite et al. (2004) used quantum chemistry to investigate three possible fates of the BrHg radical, namely, the addition of O₂, Br, and OH (all assumed to be barrierless). While BrHgOO was computed to be too unstable to be of interest, the reactions of BrHg with OH or Br were found to form thermally stable compounds. They also computed a rate constant for BrHg + Br → HgBr₂. A sophisticated computational study by Balabanov et al. (2005) confirmed that this reaction was barrierless and obtained a very similar value for its rate constant.

Concentrations of OH and Br are quite low in most of the troposphere, even compared to many other radicals. It is important to note that no previous research has considered the reaction of BrHg or ClHg with radicals other than OH and Br. We assume, as did Goodsite et al. (2004), that reactions of BrHg and ClHg with other radicals are barrierless. This assumption is not tested in the work to be presented here; rather, we investigate the stability of BrHgY and ClHgY compounds, where Y are relatively abundant atmospheric radicals. The goal is to determine if species other than OH and Br are likely to remove BrHg and ClHg. The potential for such reactions is important for BrHg, because it is thermally unstable. At 298 K and 1 atm of air, its computed lifetime with respect to dissociation is only about 10 seconds (Goodsite et al., 2012). While BrHg lives longer at the lower temperatures and pressures prevalent in the middle and upper troposphere, dissociation of BrHg will often outcompete reaction with OH or Br. If more abundant radicals than OH and Br can react with BrHg, then the modelled lifetime of Hg(0) in the atmosphere would decrease, and the range of conditions under which Br is computed to oxidize Hg(0) to Hg(II) could be greatly broadened.

Below we outline the methods used for quantum chemical calculations, followed by the results of these calculations for the bond energies for BrHgY and ClHgY compounds, where Y are NO, NO₂, O₂, HO₂, BrO, and ClO. Although the ClHgY compounds may be less generally important than the BrHgY compounds, they are likely important in atmospheric mercury depletion events and potentially have enormous value as models for the BrHgY compounds. The present work is aimed to inspire future experiments, and inclusion of computational results for the ClHgY compounds doubles the number of potential experiments aided by the present work. Results are presented regarding the potential for Y, especially ClO, BrO, and NO₃, to initiate the oxidation of Hg(0). As a guide to future laboratory studies of these compounds by negative ion mass spectrometry, we report electron affinities for most of these BrHgY and ClHgY compounds. Finally, we reanalyze the thermodynamics of BrHg and compute the equilibrium constant and rate constant for its dissociation as a function of temperature.

2 Computational methods

Quantum chemical calculations were carried out using the Gaussian09 system of programs (Frisch et al., 2009). Relativistic effects present challenges to accurate quantum calculations on Hg and Br, so effective core potentials (ECPs) were used. Calculations on Hg employed a fully relativistic ECP, referred to as ECP60MDF; this substitutes for the innermost 60 of Hg's 80 electrons (Figgen et al., 2005). The outer 20 electrons are treated with the aug-cc-pVTZ correlation consistent basis set developed by Peterson and Puzarini (2005) for use with this ECP. The fully relativistic ECP10MDF substituted for the 10 innermost electrons of Br, and the corresponding aug-cc-pVTZ basis set was used for the remaining 25 electrons (Peterson et al., 2003). Other atoms were treated with the aug-cc-pVTZ of Dunning and coworkers for all electrons (Dunning, 1989; Kendall et al., 1992; Woon and Dunning, 1993; Davidson, 1996). For simplicity, we refer to this combination of basis sets as aVTZ.

Geometries of all molecules, ions, and radicals were first optimized using density functional theory, specifically the hybrid exchange functional of Becke (1993) and the correlation functional of Lee et al. (1988), a combination denoted B3LYP. Calculations for free radicals were carried out with the spin-unrestricted formalism. Harmonic vibrational frequencies were computed using analytical second derivatives, and all species were verified to be local minima. Unscaled harmonic vibrational frequencies were used to determine zero-point vibrational energies. The energies at the B3LYP geometries were recalculated using coupled cluster theory with single and double excitations (CCSD), and using CCSD plus a quasiperturbative treatment of connected triple excitations, denoted as CCSD(T) (Ragavachari et al., 1989). CCSD and CCSD(T) calculations were carried out with the same aVTZ basis set as used for the B3LYP calculations. The *T*₁ diagnostic of Lee and Taylor (1989) was used to check whether CCSD and CCSD(T) calculations are likely to be reliable. Calculations of the equilibrium constant for BrHg dissociation were carried out using the *thermo* portion of the MultiWell program package of Barker (2001, 2011), and values at two temperatures were recomputed by hand to verify results.

3 Results and discussion

3.1 Thermodynamic stability of XHgY species for X = (Cl, Br)

Figure 1 shows the structure of HgCl₂, HgBr₂, and the BrHgY species; Cartesian coordinates of all Hg compounds are reported in the Supplement. We include HgBr₂ and HgCl₂ for the purpose of comparing our B3LYP-computed structures with previous experimental results (Kashiwabara et al., 1973; Deyanov et al., 1985) and the highly refined

Table 1. XHg-Y bond energies in kJ mol^{-1} at a temperature of 0 K at several levels of theory, including zero-point energy corrections at B3LYP/aVTZ. CCSD and CCSD(T) results are based on single point energies using B3LYP/aVTZ structures. For $Y = X, \text{NO}, \text{NO}_2, \text{O}_2, \text{HO}_2, \text{BrO},$ and ClO . Selected results from the previous literature are given in parentheses.

Y	X = Br			X = Cl		
	B3LYP	CCSD	CCSD(T)	B3LYP	CCSD	CCSD(T)
-X	280.3	303.1	314.8 (305.4) ^a (301 ± 45) ^b	315.0	324.9 (344 ± 16) ^b	337.0 (350.6) ^a
-NO	37.2	18.3	49.2	44.6	24.8	54.4
-ONO	112.3	156.1	160.5	119.7	160.6	165.0
-NO ₂	115.4	139.0	148.9	122.3	143.5	153.4
-OO	17.5	13.7	27.9	23.4	19.4	33.0
-OOH	136.9	160.6	177.6	145.0	166.4	183.1
-OBr	183.8	217.4	232.6	191.0	221.9	237.0
-OCl	177.4	205.9	220.6	184.8	210.5	225.1

^a CCSD(T) calculations of Balabanov and Peterson (2003b)

^b Chase et al. (1998).

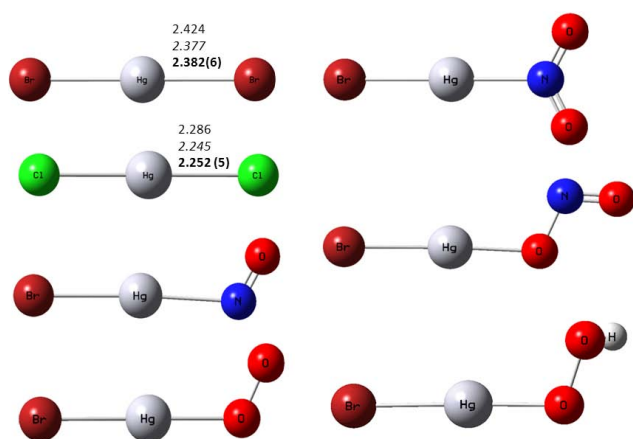


Fig. 1. Structures of various BrHgY molecules and HgCl₂ with BrHg-Y bond lengths in Ångströms. For HgBr₂ and HgCl₂ we also report bond lengths calculated by Balabanov and Peterson (2003a, in italics) and values from experiment (Deyanov et al., 1985 and Kashiwabara et al., 1973) in bold. Numbers in parentheses are 2 s.d. of the experimental bond length.

results of Balabanov and Peterson (2003a), who extrapolated CCSD(T) structures to the basis set limit and included corrections for relativistic and core-valence effects. While the previous computational results are in good to excellent agreement with experiment, the present method yields bond lengths that are 0.02–0.05 Å too long. To determine the extent to which computed bond energies are underestimated as a result of this difference in bond lengths, the CCSD(T)/aVTZ energy was recomputed at the CCSD(T)/aVTZ geometries reported by Balabanov and Peterson (2003a). The resulting underestimates are 8.6 kJ mol^{-1} for HgCl₂ and 11.1 kJ mol^{-1} for HgBr₂. These errors are too small to change the atmospheric significance of our results.

Table 1 lists XHg-Y bond energies for a number of species at different levels of theory. NO₂ has radical character at both N and O, resulting in two potential motifs for bonding with XHg; these are distinguished by being labelled -NO₂ and -ONO, respectively. First, we evaluate the internal consistency of our calculated bond energies. The CCSD and CCSD(T) bond energies are in good agreement, with the CCSD results differing from the CCSD(T) results by amounts ranging from -4 to -31 kJ mol^{-1} . The largest differences are for the weakly bound XHg-NO species; excluding these, the largest deviation is -17 kJ mol^{-1} (for XHgOOH). The T_1 values (listed in the Supplementary Data) scarcely exceed 0.030 for radicals or 0.020 for closed-shell species, further supporting the reliability of CCSD(T) for these molecules (Lee and Taylor, 1989). In spin-unrestricted B3LYP calculations on spin 1/2 species, the value of $\langle S^2 \rangle$ deviates by no more than 0.011 from the canonical value of 0.75, indicating spin contamination is not a significant problem.

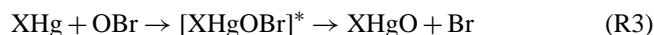
Turning to experiment, the only bond energies available are for HgBr₂ and HgCl₂. As shown in Table 1, the present results agree well with experiment for both compounds, although the large experimental uncertainty for HgBr₂ prevents rigorous evaluation. The present values also agree within 14 kJ mol^{-1} with the best values of Balabanov and Peterson (2003b). B3LYP calculations consistently underestimate the CCSD(T) bond energies by 40–50 kJ mol^{-1} except for the weakly bound XHgO₂ and XHgNO species. Our BrHg-O₂ bond energy of 28 kJ mol^{-1} computed with CCSD(T) energies is in surprisingly good agreement with the 30 kJ mol^{-1} value reported by Goodsite et al. (2004) using B3LYP. XHg binds somewhat more strongly with the O-atom than the N-atom of NO₂. The XHg-OCl and XHg-OBr bonds are computed to be much stronger than any of the other XHg-Y bonds.

Table 2. XHgOX' bond energies (kJ mol^{-1}) at a temperature of 0 K using CCSD(T)/aVTZ single point energies computed with B3LYP/aVTZ structures and zero-point energy corrections.

X	X'	X - HgOX'	XHg-OX'	XHgO-X'	(XHg-OX' - XHgO-X')	
					this work	literature ^a
Br	Br	300.2	232.6	224.0	9	16
	Cl	291.3	220.6	219.0	2	-15
Cl	Br	317.2	237.0	222.0	15	24
	Cl	308.3	225.1	217.0	8	-5

^a The literature value is computed from the differences in bond energies at 0 K for XHg-O (250 kJ mol^{-1} for X = Br and 260 kJ mol^{-1} for X = Cl from Balabanov and Peterson (2003b)) minus that for O-X' (234 kJ mol^{-1} for BrO from Kim et al. (2006); 265 kJ mol^{-1} for ClO from Coxon and Ramsay (1976)).

For $Y = \text{OX}'$ (=OCl or OBr), the strength of all bonds was determined. As reported in Table 2, the X-HgOX' bond is by far the strongest. Switching X and/or X' between Cl and Br changes bond energies only modestly (no more than 26 kJ mol^{-1}). The XHg-OX' bonds are similar in strength to the XHgO-X' bonds; the accuracy of the relative values of these two bond energies is reasonably good as measured against the results obtained combining the values of Balabanov and Peterson (2003b) with experimental X-O bond energies (Kim et al. 2006; Coxon and Ramsay, 1976). The thermodynamic values from the literature imply the following type of reaction might occur via a chemically activated intermediate (marked with *):



A full evaluation of the competition between quenching and chemically activated decomposition of XHgOBr is beyond the scope of this work.

The XHg-O₂ and XHg-NO bond energies are sufficiently small that we can expect them to dissociate rapidly. For example, if one assumes the Arrhenius pre-exponential factor, *A*, for dissociation is as low as 10^{13} s^{-1} , then ClHgNO, the most-stable of these four species, has a computed lifetime of only 2 seconds at 200 K. The remaining XHgY compounds exhibit much stronger bonding and will not undergo thermal dissociation under atmospheric conditions. The kinetics of XHg + Y reactions might be expected to differ only modestly with the nature of Y; Holmes et al. (2006) explicitly assumed that the rate constant for the BrHg + OH reaction was the same as that for BrHg + Br. If this assumption is approximately accurate, the concentration of Y will be the dominant factor controlling which Hg(II) species are formed upon the halogen atom-initiated oxidation of Hg(0). Thus, one would expect reaction with NO₂ to be the dominant fate of XHg in the free troposphere and stratosphere. In remote regions of the troposphere, HO₂ will compete with NO₂, and will possibly become a dominant reaction partner for BrHg. In the springtime Arctic and some marine environments, BrO (and, perhaps, ClO) will likely be important reaction partners for ClHg and BrHg as reported in previous studies (e.g., Brooks

et al., 2006; Obrist et al., 2011). The reported high concentration of Br in the springtime Arctic (Stephens et al., 2012) means that ClHg and BrHg might also react with Br in this particular environment. However, in most regions of the atmosphere XHg will react mostly with NO₂ and HO₂; these reactions are omitted from current models of Hg(0) oxidation.

3.2 Thermodynamic stability of HgY

Based on the broad survey of Cremer et al. (2008) it appears that very few radicals bond to Hg(0) with enough strength to form thermally stable XHgY at room temperature. Nevertheless, it seemed worthwhile to investigate whether any of the radicals, Y, studied in this work could initiate Hg(0) oxidation. Spicer et al. (2005) reported rate constants for reactions of ClO and BrO with Hg(0), and Raofie and Ariya (2004) observed reaction between BrO and Hg(0) in a chamber experiment. Of particular interest, recent modeling of field data during a mercury depletion event in the Dead Sea region (Tas et al., 2012) led to the conclusion that BrO was responsible for initiating much of the oxidation of Hg(0). Formation of BrHgO via the reaction:



requires insertion of an unreactive Hg atom into a Br-O bond of non-negligible strength ($\sim 238 \text{ kJ mol}^{-1}$), and has been found to have so high an activation barrier ($\sim 150 \text{ kJ mol}^{-1}$) as to be kinetically unfeasible (Balabanov et al., 2005). More likely possibilities are compounds with structures HgBrO and HgOBr. The former was computed to have an Hg-BrO bond energy of about 80 kJ mol^{-1} (Balabanov and Peterson, 2003b). Here we consider the structures HgOBr and HgOCl, which have not been studied to date.

Our calculations obtain a slightly negative binding energy (-1 kJ mol^{-1}) for Hg-OBr (see Table 3). This negative value is most likely an artefact of evaluating the CCSD(T) energy at B3LYP geometries; as noted in Sect. 3.1 for HgCl₂ and HgBr₂, this can easily result in underestimating bond energies by $\sim 10 \text{ kJ mol}^{-1}$. The computed binding energy for Hg-OCl is 2 kJ mol^{-1} . We interpret the results to mean

Table 3. Hg–Y bond energies (kJ/mol) at a temperature of 0 K using CCSD(T)/aVTZ single point energies computed with B3LYP/aVTZ structures and zero-point energy corrections (negative sign indicates dissociation to Hg + Y is computed to be energetically favored). For Y = ClO and BrO, only the isomer with bonding between the oxygen and mercury was considered (see text).

-Y	Bond energy
-OCl	2.2
-OBr	−0.8
-ONO ₂	20.8
-OOH	2.1

Table 4. XHgY electron affinities (EA, eV) and reaction energies for anion dissociation (E_{rxn} , kJ mol^{−1}) at a temperature of 0 K using CCSD(T)/aVTZ single point energies computed with B3LYP/aVTZ structures and zero-point energy corrections. A negative number indicates the fragments are more stable than the XHgY anion.

X	Y	EA	E_{rxn}		
			XHg [−] + Y	XHg + Y [−]	X + HgY [−]
Br	-Br	1.62	178.3	148.3	178.3
	-NO	2.56	3.2	293.6	398.8
	-ONO	1.81	42.2	118.3	155.3
	-NO ₂	1.92	41.3	117.4	158.8
	-OO	1.83	−88.3	167.8	182.5
	-OOH	1.29	8.6	202.2	201.0
Cl	-Cl	1.59	193.0	152.1	193.0
	-NO	2.54	2.1	296.8	414.6
	-ONO	1.82	43.3	123.8	173.3
	-NO ₂	1.90	39.4	120.0	173.9
	-OO	1.83	−87.6	172.9	200.2
	-OOH	1.24	5.1	203.0	214.4

that the binding energies are quite small, so that the HgOCl and HgOBr radicals will undergo thermal dissociation much faster than they could react with other radicals under atmospheric conditions. Gaseous BrO and ClO may still be able to initiate the homogeneous oxidation of Hg(0) via formation of bound HgBrO and HgClO, as described in the previous paragraph, but rate constants for these reactions are uncertain. We suggest modelers exercise caution in using reported rate constants for the reactions of ClO and BrO with Hg(0), because experimental observation of products in the solid phase suggests experimental rate constants may be influenced by wall-catalyzed reactions.

Field work indicated that significant oxidation of Hg(0) could be occurring at night, which led to the suggestion that NO₃ might be initiating Hg(0) oxidation (Mao and Talbot, 2012). The 21 kJ mole^{−1} bond energy of Hg-ONO₂ computed here (see Table 3) is far too small to allow this radical to react with other radicals in the gas phase prior to undergoing thermal dissociation. Our results indicate the HOO forms a very weakly-bound (2.1 kJ mol^{−1}) van der Waals complex

with Hg, which will dissociate faster than any bimolecular reaction would occur.

Efforts to find geometries of HgY compounds using B3LYP failed for Y = NO, -NO₂, -ONO. Although we expect such radicals can exist, it seems likely that they are so weakly bound as to be atmospherically irrelevant.

3.3 Electron affinities of XHgY species and stability of their anions

Chemical ionization mass spectrometry (CIMS) has been a powerful tool for laboratory and field studies of trace gases. In the hopes of providing experimentalists a tool for identifying XHgY species, we computed electron affinities (EA) of the XHgY species (excepting Y = ClO and BrO) and the stability of the resulting XHgY anions. Computational results are listed in Table 4. Unfortunately, EA values are rather low: less than 2.6 eV for all XHgY and less than 2.0 eV for the stable XHgY. This is lower than the EA of the neutral analogs of commonly used anionic Cl reagents (I[−], CF₃O[−]), which means that simple electron transfer reactions from these reagent anions will not ionize the XHgY species. The low electron affinity of O₂ means that it is a viable CI reagent with all XHgY whose EA we have studied. However, as can be seen in Table 4, some of the XHgY anions are unstable, or only very slightly stable, with respect to forming XHg[−] + Y. This means that CIMS with electron transfer ionization may not be able to distinguish among many XHgY species.

3.4 Thermodynamic and kinetic analysis of the stability of BrHg

If our results in section 3.1 are correct, then the abundance of NO₂ and HO₂ in the global troposphere implies that BrHg is much more likely than previously thought to form stable compounds instead of dissociating. Some might object that present models (e.g., Kim et al., 2010; Holmes et al., 2009, 2010; Sprovieri et al., 2010b) of the Br-initiated oxidation account reasonably well for the lifetime of Hg(0); therefore, the increase in the modelled loss rate of Hg(0) implied by the results of Sect. 3.1 would violate a basic constraint on the Hg budget. This argument would carry more weight if current models were using a reliable rate constant for BrHg dissociation. In fact, as we will show, the expression used in models underestimates the rate constant for BrHg dissociation by a factor of 21 at 298 K.

The thermal dissociation of BrHg



is explicitly included in models of Br-initiated oxidation of Hg(0). The rate constant for this reaction, $k_{-1}(T)$, is commonly computed from the values of $k_1(T)$ determined experimentally by Donahoue et al. (2006) and the equilibrium constant, $K_{\text{eq}}(T)$, of Reaction (R1). The value of $K_{\text{eq}}(T)$ is usually taken to be that implied by the results of Goodsite

Table 5. Recommended equilibrium constant, $K_{\text{eq}}(T)$, for $\text{Br} + \text{Hg} \rightarrow \text{BrHg}$ as a function of temperature for two standard states.

T (K)	K_{eq} (standard state)	
	(1 molecule cm^{-3})	(1 bar)
200	1.25×10^6	3.48×10^{-14}
210	8.02×10^6	2.35×10^{-13}
220	4.35×10^7	1.34×10^{-12}
230	2.04×10^8	6.55×10^{-12}
240	8.38×10^8	2.81×10^{-11}
250	3.08×10^9	1.08×10^{-10}
260	1.02×10^{10}	3.72×10^{-10}
270	3.10×10^{10}	1.17×10^{-9}
280	8.70×10^{10}	3.41×10^{-9}
290	2.27×10^{11}	9.21×10^{-9}
298	4.67×10^{11}	1.95×10^{-8}
300	5.55×10^{11}	2.33×10^{-8}
310	1.28×10^{12}	5.56×10^{-8}
320	2.81×10^{12}	1.26×10^{-7}

et al. (2004). Unfortunately, their results were heavily biased by an inaccurate literature value of the Br-Hg bond energy. We computed $K_{\text{eq}}(T)$ based on the more reliable data of Tellinghuisen and Ashmore (1983). The complete set of data used for calculation of $K_{\text{eq}}(T)$ are provided in Supplement. The equilibrium constant has been calculated as an average over the isotopologues using the isotopic mass and abundance data of de Laeter et al. (2003).

The resulting equilibrium constant for reaction (1) is reported in Table 5. It is well fit (to within the uncertainty in the Arrhenius pre-exponential terms) by the expressions:

$$K_{\text{eq}}(T)(\text{cm}^3 \text{ molecule}^{-1}) = (9.14 \pm 0.06) \times 10^{-24} \times \exp\{(+7801 \pm 201)/T\} \quad (1a)$$

$$K_{\text{eq}}(T)(\text{bar}^{-1}) = (2.19 \pm 0.015) \times 10^{-4} \times (298/T) \times \exp\{(+7802 \pm 201)/T\} \quad (1b)$$

where reported uncertainties are 2 s.d. The dominant source of uncertainty arises from the spectroscopic value of the bond energy, and this factor appears in the exponential terms of Eqs. (1a) and (1b). A 2 s.d. uncertainty of 0.5 cm^{-1} in the harmonic vibrational frequency and 0.01 \AA in the bond length (assumed) causes the small uncertainty reported in the pre-exponential terms. The total uncertainty in $K_{\text{eq}}(T)$ is $\pm 62\%$ at 298 K and $\pm 77\%$ at 200 K.

The experimental rate constant of Reaction (R1) reported by Donahoue et al. (2006) was at or near the low pressure limit with a value of:

$$k_1(T) = (1.46 \pm 0.34) \times 10^{-32} \times (T/298)^{-(1.86 \pm 1.49)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (2)$$

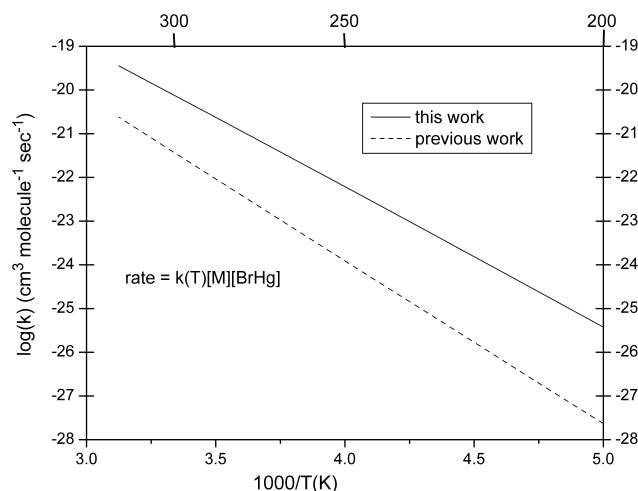


Fig. 2. Illustration of the temperature dependence of the rate constant for BrHg dissociation. The rate constant for dissociation is first order in $[\text{BrHg}]$ and first order in $[\text{M}]$. Both values displayed use $k(\text{BrHg} + \text{M} \rightarrow \text{Br} + \text{Hg} + \text{M})$ from Donahoue et al. (2006), but the previous work relies on the equilibrium constant implied by the work of Goodsite et al. (2004).

over the range $243 \text{ K} \leq T \leq 293 \text{ K}$ and pressures up to 600 Torr. Assuming that this rate constant is in the low-pressure limit for all atmospherically relevant conditions, one can use the following equation:

$$k_{-1}(T) = k_1(T)/K_{\text{eq}}(T) \quad (3)$$

to arrive at an expression of the rate constant for BrHg dissociation under atmospheric conditions:

$$k_{-1}(T) = (1.60 \pm 0.37) \times 10^{-9} \times (T/298)^{-(1.86 \pm 1.49)} \times \exp\{(-7801 \pm 201)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

where the rate of Reaction (R-1) equals $k_{-1}(T)[\text{BrHg}][\text{M}]$. The resulting value of k_{-1} is higher than the value of Goodsite et al. (2004) by a factor of 21 at 298 K and 160 at 200 K; this startling difference is depicted in Fig. 2. Combining the experimental results of Donahoue et al. (2006) with the equilibrium constant implied by Goodsite et al. (2004) leads to an error in k_{-1} of a factor of 65 at 298 K. It is clear that previous work greatly underestimated the rate of dissociation (overestimated the stability) of HgBr. Very recently, Goodsite et al. (2012) revised their value of $k_{-1}(T)$ using, in part, the bond energies from Tellinghuisen and Ashmore (1983) and Shepler et al. (2007). Their new result at 1 atmosphere is:

$$k_{-1}(T) = 4.0 \times 10^9 \exp(-7292/T) \text{ s}^{-1} \quad (5)$$

which is only 1.6–2.3 times higher than the value recommended here (Eq. 5) over the range 200–320 K.

4 Conclusions

Present models of the Br-initiated oxidation of Hg(0) are shown to be significantly incomplete in describing the fate of the BrHg radical, because they do not include the most likely reactions of that radical. Reaction with NO₂, HO₂, ClO and BrO are suggested to be much more important than reaction with OH or Br for most of the atmosphere. In addition, the rate constant for thermal dissociation of BrHg is found to be significantly lower than previously calculated. Revision of models of atmospheric mercury are likely to result in significant changes in predicted rates of Hg(0) oxidation in different geographical regions and different parts of the atmosphere. These changes may have significant consequences for model predictions of the temporal and spatial distribution of RGM deposition. HOO, NO, NO₂, and NO₃ are found to bind Hg(0) far too weakly to initiate its oxidation in the gas phase.

The XHgY compounds with Y = NO₂, HOO, ClO, and BrO are expected to dominate Br-initiated RGM formation in the free troposphere. Formation of this RGM is limited by three factors:

1. the rate of BrHg formation
2. the rate of BrHg dissociation, in competition with
3. the abundance of radicals, Y, to enable XHgY formation.

The abundance of Br is extremely low, and this is recognized as a major limiting factor in the rate of BrHg formation. The concentration Br is believed to be largest in the upper troposphere in the polar regions, but the upper troposphere is coldest at the equatorial tropopause. Low temperatures lead to a higher rate constant for BrHg formation and a lower rate constant for BrHg dissociation. The balance between the concentration of Br and temperature effects on the ability of BrHg to go on to form RGM will be a major control on the rate of Br-initiated formation of RGM.

Based on the factors discussed above, one might expect there exist optimal conditions for RGM formation in the global troposphere. A number of measurements from mid-latitudes suggest that RGM is more abundant in the mid-troposphere than at lower altitudes (Landis et al., 2005; Swartzendruber et al., 2006; Lyman and Jaffe, 2012). Global field measurements are needed to quantify the distribution of RGM to understand RGM formation mechanisms.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/12/10271/2012/acp-12-10271-2012-supplement.pdf>.

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