Calculation of the Energetics for Oxidation of Gas-Phase Elemental Hg by Br and BrO

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Recently, depletion of gas-phase elemental Hg has been observed by several research groups after polar sunrise in the atmospheric boundary layer in Arctic regions. At the same time Hg compounds have been observed to accumulate in the polar snowpack. Several different oxidation reactions involving gas-phase Br and BrO have been hypothesized to explain this process. Molecular quantum mechanical methods are here applied to evaluate the energetics of such reactions, in both the gas phase and aqueous solution. The formation of HgO from the reaction of Hg^0 and BrO in the gas phase is found to be endothermic, but HgBr and $HgBr_2$ can form exothermically through the oxidation of Hg^0 by either Br atom radicals or Br_2. The instability of HgO has the same cause as the low stability of HgBr compared to $HgBr_2$, i.e., the high first IP of Hg. The calculations also indicate that $HgBr_2$ is stable photolytically, while gas-phase HgO and HgBr are decomposed by visible light.

Introduction

Gas-phase elemental Hg (GEM) has both natural and anthropogenic sources. In the atmosphere elemental gas-phase Hg^0 undergoes long-range atmospheric transport. Several recent studies indicate that GEM is rapidly oxidized to Hg(II) compounds, known as reactive gaseous mercury (RGM), in Arctic regions after polar sunrise.[1−4] The reduction in GEM is correlated with a reduction in surface O_3 concentration, which is thought to be caused by photochemically initiated catalytic reactions involving halogen species, particularly Br and BrO.[2] The oxidizing agents for GEM are also thought to be predominantly halogen atoms or halogen oxide free radicals. Modeling of the kinetics and energetics of the process[5−8] has been carried out previously using experimental heat of formation data on assumed reactants and products. Experimental studies have determined the rate of loss of Hg^0 in the presence of various oxidants, but in some cases the products were not clearly identified.[9−11] Ariya et al.[11] noted that experimental data on the gaseous reactions of Hg^0 are very limited, compared to the extensive data on the solution chemistry of Hg. This is due to the small concentrations of species under atmospheric conditions, the low volatility of products, and the strong effects of water vapor and surfaces on the reaction kinetics.

There is only limited experimental information on the structure and stability of HgO and HgBr.[12,13] Fortunately, the structures and stabilities of the Hg(II) dihalides are better known, from both experiment and calculation.[14] There have been a number of calculations of the properties of Hg compounds within the theoretical inorganic literature.[15,16] In a recent, very accurate study[15e] the gas-phase species HgO was found to be stable with respect to Hg^0 and ground state O by only 4 kcal/mol, compared to an experimental value of 53 ± 10 kcal/mol.[12c] These results cast considerable doubt on the experimental value. The gas-phase reaction of BrO with HBr has also been studied at a high level of theory[17] and thus provides a benchmark for the accuracy of the present study. The structures and properties of Hg-containing species in aqueous solution have also been studied using theoretical methods.[18]

It is desirable to characterize the energetics for some of the possible gas-phase and aqueous solution oxidation reactions of Hg^0 using modern quantum mechanical techniques. Spectral properties of these species have also been evaluated, to determine their photochemical stability and to assist in their characterization.

Computational Methods

Standard methods of molecular quantum mechanics have been used, specifically the Hartree−Fock (HF) method, the Moller−Plessett many-body perturbation theory method to second order (MP2), the quadratic configuration interaction method with single and double substitutions (QCISD), and the coupled cluster with single, double, and perturbative triple substitutions (CCSD(T)). All these methods are described in standard computational chemistry monographs[19] The MP2, QCISD, and CCSD(T) methods incorporate correlation in the motion of electrons,[20,21] which is neglected at the HF level. They typically provide much more accurate bond energies and somewhat better equilibrium geometries than does the HF method. However, they are more demanding of computer time than HF, particularly the QCISD and CCSD(T) methods. The basis sets used to expand the molecular orbitals were of valence electron only, relativistic effective core potential type,[22] which are here designated SBK, with added polarization functions on all the atoms. For Hg single f polarization functions with an exponent of 0.486 (from ref 16) are employed. For all the species considered equilibrium geometries in the gas phase have been determined at HF, MP2, QCISD, and CCD levels. Additional CCSD(T) calculations have been done at the CCD equilibrium geometries, since no analytical gradients were available for CCSD optimizations in the software available. For HgO and HgBr it was established by numerical search that the optimized CCSD(T) energies and the CCSD(T)/CCD energies differed by less than 0.1 kcal/mol. Vibrational frequencies, zero-point vibrational energies (ZPE), and vibrational, rotational, and translational (VRT) contributions to the gas-phase enthalpy and free energy at 25 °C have been calculated at the HF level, for all species except HgOH (see below). The necessary equations for the ZPE and VRT contributions[23] are incorporated into the quantum chemical software. For HgOH alone a significant difference in equilibrium bond length, vibrational frequency, and vibrational contribution

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TABLE 1: Possible Reactions of Elemental Gas-Phase Hg^0 and Related Species (energies in kcal/mol)[a]

	ΔE_g						
reaction	(U)MP2	QCISD	CCSD(T)/CCD	ΔE_{ZPE}	ΔH_{VRT}	ΔG_{VRT}	ΔG_{tot}
$Hg + BrO \Rightarrow HgO + Br$	+39.9	+47.1	+49.5	−0.6	−0.4	−0.5	+49.0
$Hg + 2Br \Rightarrow HgBr_2$	−83.9	−78.6	−80.7	+0.9	+0.2	+13.1	−67.6
$Hg + BrO \Rightarrow HgBr + O$	+26.9	+27.1	+29.2	−0.8	−1.7	−0.7	+28.5
$Hg + Br_2 \Rightarrow HgBr_2$	−43.5	−41.4	−41.2	+0.4	+0.3	+7.4	−33.8
$Hg + Br \Rightarrow HgBr$	−11.3	−12.3	−12.9	+0.3	−0.2	+4.9	−8.0
$HgBr + Br \Rightarrow HgBr_2$	−72.6	−66.3	−67.8	+0.6	+0.4	+8.1	−59.7
$Hg + O(^3P) \Rightarrow HgO$	+1.8	+9.9	+7.3	+0.5	−0.2	+5.1	+12.4
$Hg + O_3 \Rightarrow HgO + O_2$	+29.4	+10.3	+19.8	−2.1	−1.6	−3.2	+16.6
$HgO + H_2O \Rightarrow Hg(OH)_2$	−68.4	−66.6	−67.1	1.9	+0.6	10.6	−56.5
$Hg + OH \Rightarrow HgO + H$	+98.8	+92.2	+103.9	−5.2	−4.9	−5.4	+98.5
$Hg + OH \Rightarrow HgOH$	−15.7	−7.0	−7.3	+1.8	+0.8	+6.3	−1.0
$Hg + 2\,OH \Rightarrow Hg(OH)_2$	−89.5	−75.6	−78.1	+5.2	+3.0	+19.1	−59.0
$Hg + H_2O_2 \Rightarrow Hg(OH)_2$	−42.2	−32.1	−31.5	−1.2	−1.6	+6.1	−25.4
$Hg + Cl \Rightarrow HgCl$	−13.7	−15.4	−16.4	0.4	−0.2	+5.0	−11.4
$HgCl + Cl \Rightarrow HgCl_2$	−80.8	−74.8	−76.7	0.9	+0.5	+8.5	−68.2
$BrO + HBr \Rightarrow Br + HOBr$	−23.0	−12.7	−13.7	+3.6	+3.3	+4.8	−8.9

[a] Gas-phase energetics calculated at MP2, QCISD, and CCSD(T)/CCD levels. Vibrational energies calculated at the HF level (unscaled), except for HgOH, evaluated at MP2.

to the gas-phase enthalpy and free energy was found between HF and MP2 levels, and so the MP2 values of these quantities have been used for HgOH.

To approximate hydration energies, the COSMO (conductor-like screeening MO method[24]) version of the self-consistent reaction field polarizable continuum method has been used. This is a very rapid and efficient technique that utilizes a nonspherical cavity about the solute and gives results very similar to those from older nonspherical cavity polarizable continuum models, but at much less computational cost. Nonetheless it still suffers from the main ambiguity of polarizable continuum models: the lack of uniqueness in the choice of the solute cavity. It is important to realize that any polarizable continuum model of hydration involves very serious approximations and that the hydration energy differences evaluated for reactions, particularly those involving ions, are invariably much less accurate than are the corresponding gas-phase energies. The quantum chemical software GAMESS[25] and GAUSSIAN 94 and GAUSSIAN98[26,27] have been used for the calculations.

To evaluate visible−UV excitation energies and intensities, the configuration-interaction singles method (CIS[28]), the time-dependent Hartree−Fock method (TD HF),[29] and the time-dependent density functional method (TD DFT[30]) have been used. The DFT studies have been done using the hybrid B3LYP potential.[31] Analyses of these different methods for calculating excitation energies are given in refs 30a,b. Basically, CIS describes the excited state wave function at a level comparable to Hartree−Fock, using single excitations from the HF determinant. The TD HF method (also called the random phase approximation, RPA) includes some double excitations, giving a slightly correlated description of both ground and excited states, while TD DFT includes additional electron correlation through the exchange−correlation potential. It was found in ref 30a for several different molecules that TD DFT using the hybrid B3LYP potential gave the best agreement with experiment, consistently giving excitation energies intermediate between those from TD HF and TD DFT with pure DFT potentials.

Results and Discussion

Calculated energetics for gas-phase reactions involving Hg^0 oxidation are given in Table 1. Values are given for the change in electronic energy, ΔE_g, at the MP2, QCISD, and CCSD(T)/CCD levels, the change in zero-point vibrational energy, the change in the vibrational, rotational, and translational components of both the enhalpy and the free energy (both evaluated at the HF level, except for HgOH), and the total change in gas-phase free energy (which equals the CCSD(T)/CCD value of ΔE_g plus ΔG_{VRT} at 25 °C). In most cases the ΔE_g term dominates the free energy change, although the ΔG_{VRT} value is not negligible when there is a change in number of moles in the reaction. The results obtained using the QCISD and CCSD(T)/CCD methods are quite similar, usually differing by 2 kcal/mol or less (except for some reactions involving HgO), as expected on the basis of the similar formalisms of the methods.

It is clear from the data in Table 1 that the reaction of Hg^0 with BrO is predicted to be endoergic by a considerable amount, whether the reaction product is HgO or HgBr. This is particularly true for the HgO product, which is calculated to be unbound with respect to gas-phase Hg^0 and $O(^3P)$ by 12.4 kcal/mol in free energy. HgBr is calculated to be stable, but by only 8.0 kcal/mol in free energy.

As noted before, early quantum mechanical studies[15a] on gas-phase HgO also found it to be *unbound* with respect to Hg^0 and $O(^3P)$ (by about 14 kcal/mol), while the experimental data indicated that it was *bound* by 53 ±10 kcal/mol, a discrepancy on the order of 60 kcal/mol. The experimental results[12c] were obtained using the "third-law method" and involved assumptions about the species present in the vapor over solids of composition MX (where M = Zn, Cd, Hg and X = O, S). The results of the present CCSD(T)/CCD calculations give HgO as unbound by 7.3 kcal/mol. Although a relativistic HF calculation[15d] gave HgO as bound by 40 kcal/mol, that calculation used a small basis set and did not include correlation. Very recent studies using CCSD(T) and MRCI methods with very large correlation consistent basis sets (including newly designed basis sets up to quintuple ζ for Hg), careful searches for both singlet and triplet states, and incorporation of spin−orbit corrections give HgO as bound by only 4 kcal/mol.[15e] Using the CCSD(T) method with a polarized double-ζ basis set these researchers[15e] found HgO to be unbound by about 6 kcal/mol, similar to the +7.3 kcal/mol we obtained at the CCSD(T)/CCD level with the polarized SBK bases. The very accurate studies of ref 15e thus indicate that the calculated stability of HgO is increased by around 10 kcal/mol on going from the double-ζ basis to the infinite basis set limit. This is not really a particularly large basis set effect; it seems large only because the bond energy is very close to zero. It is clear from the previous theoretical studies and our additional calculations that the experimental data indicating high stability for diatomic HgO (and much of the modeling based upon it, e.g., ref 6) are probably erroneous.

By contrast, the reactions of Hg^0 with Br atoms are exoergic, although the addition of the first Br is much less exoergic than that of the second. This difference in stability of Hg(I) and Hg(II) halide species is well established for the chlorides. The enthalpy changes for the addition of the first and second Cl atoms to Hg^0 are found experimentally to be -25.1 and -81.0 kcal/mol, respectively, while our calculated values are -16.4 and -76.7 kcal/mol. Previous theoretical values are -16.8 and about -72 kcal/mol for addition of the first and second Cl atoms, respectively.[15b] This resolves the problem of the apparent termolecular character of eq 2, with two Br atoms adding to Hg. In fact, this process can occur in two steps which are both exoergic. The ground state of HgBr has the correct symmetry to dissociate to Hg and Br atoms in their ground states, and there is no energy barrier (as is usually the case for reactions involving free radicals). This indicates that both HgBr and $HgBr_2$ may be produced in the atmosphere. In their studies of the reaction of Hg^0 with Br and Br_2 Ariya et al. (ref 11) found $HgBr_2$ as the major product absorbed on the walls of the reaction vessel. The direct reaction of Hg^0 with Br_2, while also exoergic, is not expected to be important in the atmosphere since Br_2 will be photolyzed by light in the visible region, as discussed in ref 4.

It is clear that our CCSD(T)/CCD calculations with polarized double-ζ basis sets underestimate the bond energies of the Hg(I) oxide and halides. This underestimation appears to be around 10 kcal/mol, based on comparing our calculated values with the experimental value for HgCl and the accurately calculated bond energy of HgO,[15e] for which the experimental value seems dubious. Using tabulated experimental values for the free energy changes involving the elements O, Cl, Br, and Hg (e.g., for the vaporation free energy of Hg and the dissociation free energy of O_2 and the halogens) we obtain calculated values of $+28.2$, $+26.9$, and $+81.2$ kcal/mol for $\Delta H_f{}^\circ{}_{298}$ for HgCl, HgBr, and HgO, respectively, to be compared with experimetnal values of about $+23$, $+19$, and $+20$ kcal/mol, respectively. Thus to obtain more accurate energetics, we could make the ΔG_{tot} values from Table 1 more negative by about 10 kcal/mol for those reactions in which such Hg(I) species are formed. Although this certainly changes the results quantitatively, it does not change any qualitative conclusions; for example, the formation of HgO + Br from Hg + BrO is still strongly endoergic.

Note that the very weak exothermicity for the formation of HgO and HgBr is partly a consequence of the very high first ionization energy (IE) of Hg (10.43 eV experimental, compared to 8.99 eV experimental for Cd). QCISD calculations using the relativistic effective core potential basis set augmented with Hg f polarization functions give a value of 10.04 eV for this quantity. The large first IE for Hg is mainly a relativistic effect.[16]

The reaction of Hg^0 with O_3 has been previously studied, but the identity and phase of the product are still in doubt, since the reaction was described by Hall (ref 9) as "partly heterogeneous". The present results indicate that the reaction of Hg^0 with O_3 which produces HgO and O_2 in the gas phase is endoergic by about 20 kcal/mol, but that subsequent reaction of HgO with H_2O is even more strongly exoergic, so that formation of the final product $Hg(OH)_2$ will be favorable. Studies of the reaction of Hg^0 with OH radical[10] are consistent with the production of HgOH molecules, with a slightly negative ΔG of around -6 kcal/mol based on calculations from ref 15b. The present calculations indicate a free energy change in the gas phase of only -1.0 kcal/mol for the formation of HgOH from Hg and OH, somewhat smaller than that previously calculated.[15b] By contrast, the formation of HgO and H from Hg + OH is strongly endoergic, as concluded as well in refs 10 and 15c. The reactions of Hg^0 with 2 OH radicals and with H_2O_2 are both calculated to be strongly exoergic in the gas phase, consistent with previous theoretical studies and with experiment (ref 6).

TABLE 2: Calculated and Experimental Values of Bond Distances (in Å) for HgCl, $HgCl_2$, HgBr, $HgBr_2$, and HgO (ground state doublets for HgCl and HgBr)

	R(Hg−X) calcd				
molecule	(U)MP2	QCISD	CCD	best previous calc[a]	*R*(Hg−X) expt
HgCl	2.354	2.394	2.376	2.42	2.42[b]
$HgCl_2$	2.243	2.269	2.261	2.29	2.25[c]
HgBr	2.521	2.565	2.549 (2.567[d])		2.62[b]
$HgBr_2$	2.389	2.416	2.408		2.41[c]
HgO	1.867	1.924	1.920 (1.935[d])	1.912	

[a] Reference 15b for HgCl, ref 14b for $HgCl_2$, ref 15e for HgO. [b] Reference 13b. [c] Reference 14c for $HgCl_2$, 14d for $HgBr_2$ [d] CCSD optimized value.

Also included in Table 1 are the calculated energetics for the gas-phase reaction

$$BrO + HBr \Rightarrow Br + HOBr$$

This reaction was studied at the CCSD(T) level with large all-electron basis sets in ref 17, giving a ΔH value of -9.3 kcal/mol. The calculated ΔH for this reaction at the best computational level employed in the present work (CCSD(T) at the CCD optimized geometry, with a polarized effective core potential basis) is -10.4 kcal/mol, quite similar to the value reported in ref 17 (and fairly close to the reported experimental value of -6.1 ± 1 kcal/mol). Thus, although the present computational level is not as high as that of ref 17, the results seem quite comparable. This provides a benchmark for the accuracy of the present results.

In Table 2 calculated bond distances are given for HgCl, $HgCl_2$, HgBr, $HgBr_2$, and HgO, calculated at (U)MP2, QCISD, and CCD levels and compared with previous calculations and with experiment. We see that agreement with experiment for the well-characterized HgX_2 molecules is quite good. For the HgX species, where the internuclear distances have been determined indirectly from spectral data, the agreement is reasonable, but not particularly good. It may well be that the experimental values quoted are not very accurate. For HgO we can only compare with the previous calculated value, finding good agreement (ref 15a). Note that the Hg−X distance is much longer in HgX than in HgX_2, consistent with the weak bonding of the first X atom in a species that is essentially Hg(I)X.

In Table 3 we give calculated energetics in aqueous solution for a number of reactions. Since the reactants are mainly neutral atoms and the products are usually molecules with polar character, all the reactions become more favorable in aqueous solution; that is, ΔG_{COSMO} is negative. Because of the unsymmetric charge distributions in HgBr and HgO, they are both strongly stabilized in water and their production becomes much more favorable. Nonethless, the reaction of Hg^0 with BrO to produce HgO and Br is still endoergic, even in aqueous solution. On the other hand, oxidations of Hg^0 by either BrO^- or O_3 become favorable, in agreement with experiment (ref 8). Although a hydration energy can be calculated for HgO, a more realistic model would probably have HgO actually reacting with H_2O to give $Hg(OH)_2$, since this reaction is exoergic in both gas phase (Table 1) and aqueous solution (Table 3).

TABLE 3: Possible Reactions of Elemental Hg^0 in Aqueous Solution (energies in kcal/mol)[a]

reaction	ΔE_g CCSD(T)	ΔE_{ZPE}	ΔH_{VRT}	ΔG_{VRT}	ΔG_{COSMO}	ΔG_{aq}
$Hg + BrO \Rightarrow HgO + Br$	+49.5	−0.6	−0.4	−0.5	−28.8	+17.8
$Hg + BrO \Rightarrow HgBr + O$	+29.2	−0.8	−1.7	−0.7	−12.3	+16.2
$Hg + 2\ Br \Rightarrow HgBr_2$	−80.7	0.9	0.2	+13.1	−17.1	−85.5
$Hg + Br \Rightarrow HgBr$	−12.9	+0.3	−0.2	+4.9	−13.5	−20.9
$Hg + BrO^- \Rightarrow HgO + Br^-$	+19.7	+0.3	+0.2	+0.4	−32.0	−15.3
$Hg + O_3 \Rightarrow HgO + O_2$	+19.8	−2.1	−1.6	−3.2	−27.0	−19.9
$HgO + H_2O \Rightarrow Hg(OH)_2$	−67.1	+1.9	+0.6	+10.6	+12.2	−44.3

[a] Gas-phase energy calculated at the CCSD(T)/CCD level, vibrational corrections at the HF level, hydration energies from COSMO calculations at the HF level.

TABLE 4: Calculated Energies for Two Lowest Energy Optical Transitions in HgO, HgBr, $HgBr_2$, HgCl, and $HgCl_2$ Obtained Using the Polarized SBK Basis Set and Various Methods at the Polarized SBK MP2 Geometries, Compared with Experiment Where Available[a]

	ΔE(eV)			
molecule	CIS	TD	TD B3LYP	expt[b]
HgO	1.23 (0.0023)	0.76	1.01	
	4.24 (0.3161)	3.89	4.00	
HgBr	3.27 (0.0018)	3.15	1.55	2.91
	4.07 (0.1251)	3.79	3.59	
$HgBr_2$	5.67 (0)	5.60	4.05	5.39
	6.23 (0.0418)	6.19	4.53	6.26
HgCl	4.03 (0.0001)	3.90	1.97	
	4.55 (0.0925)	4.53	3.76	
$HgCl_2$	6.80 (0)	6.74	5.04	6.20
	7.67 (0.0556)	7.62	5.77	6.85

[a] Oscillator strengths are given in parentheses for the CIS calculations. [b] References 14e,f.

In Table 4 we give the two lowest calculated optical absorption energies for the same set of molecules as in Table 2, obtained with a number of different methods and our standard polarized SBK basis sets. For the CIS calculations we also give calculated oscillator strengths. The calculated energies for both HgX_2 molecules are in the UV and are in reasonable agreement with experiment, with the CIS values lying a bit above experiment and the TD B3LYP values substantially below. Such bracketing of the experimental values by the CIS and TD B3LYP calculations has been observed before for Hg compounds (ref 18e). For the HgX species and for HgO the calculated absorption energies, even at the CIS level, are much lower than for HgX_2 and fall in the visible region. This indicates that these molecules will be unstable toward photodissociation by visible light. However, the calculated oscillator strengths for these low-energy transitions in HgO, HgCl, and HgBr are about 20 times smaller than those for the fully allowed transitions, which occur in the 6−7 eV range in the Hg(II) dihalides. Optimization of the geometry in the lowest excited state using the CIS method gives Hg−X or Hg−O bond distances larger than 5 Å for these species, consistent with dissociation. Thus, such molecules would photodecompose to form Hg^0 in the atmosphere.

The present calculations indicate that all the possible reactions of BrO with gaseous Hg^0 are endoergic, particularly the one producing gaseous HgO. The experimental data indicating a large positive dissociation energy for gaseous HgO (and the modeling based upon that data) are erroneous. On the other hand, the reactions of gaseous Hg^0 with either one or two Br radicals are exoergic. The probable compound first formed in reactive gaseous mercury (RGM) is $HgBr_2$. This compound is also stable photolytically in sunlight, while species such as HgO and HgBr will decompose in visible light. Another possibility is that HgO, initially formed endoergically, can react with H_2O to form stable $Hg(OH)_2$, in either gas phase or aqueous cluster or solution. We have also carried out additional calculations on Hg_2O_2, although only at the MP2 level, that indicate that this dimer is considerably more stable than two HgO diatomics. Thus, oligomerization of the HgO may be another possible pathway to a stable product.

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