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Mercury and Reactive Halogens: The Thermochemistry of Hg + {Cl_2, Br_2, BrCl, ClO, and BrO}

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Accurate reaction enthalpies have been calculated using the CCSD(T) method and sequences of correlation consistent basis sets for the reactions of Hg with a series of small halogen-containing molecules (Cl_2, Br_2, BrCl, ClO, and BrO). Explicit extrapolations to the complete basis set limit are used together with accurate treatments of core−valence correlation, scalar relativity, and spin−orbit effects in order to predict both reaction enthalpies of the title reactions and heats of formation of the intermediates ($HgCl_2$, $HgBr_2$, HgBrCl, HgClO, and HgBrO) to an estimated accuracy of approximately 1 kcal/mol. All of the intermediates are predicted to be strongly bound and the structures and vibrational frequencies of HgClO and HgBrO are reported for the first time. The present results are expected to be useful in modeling the gas-phase oxidation of mercury in the troposphere by halogen-containing species.

I. Introduction

Because of its high biological toxicity and long atmospheric residence time, mercury is considered to be a high priority among environmental pollutants. In the atmosphere mercury is present nearly exclusively in the gas phase and in its elemental, zerovalent form, but the amount of data on its gas phase reactivity is surprisingly scarce. Recently the contamination of the arctic ecosystem by mercury has been of particular concern. Measurements of total gaseous mercury (TGM) in the arctic troposphere have shown a strong correlation between near total depletion of surface level ozone and significant drops in TGM (with concomitant deposition onto the snowpack) in the first 3 months of the arctic spring.[1] Given that halogen-catalyzed reaction cycles are thought to be responsible for the springtime depletion of tropospheric ozone,[2] reactions of reactive halogen species, e.g., Br, BrO, and ClO, with gaseous mercury have been proposed to be responsible for the greatly decreased atmospheric residence time of mercury during this period.[3] Recently similar mercury depletion events (MDEs) have also been observed in the Antarctic troposphere.[4]

Since UV radiation appears to be a necessary prerequisite for the observed mercury depletion events, the oxidation of gaseous Hg to more reactive forms might conceivably involve reactions such as

$$\mathrm{Hg} + \mathrm{X} \rightarrow \mathrm{HgX} \qquad (1)$$

$$\mathrm{HgX} + \mathrm{Y} \rightarrow \mathrm{HgXY} \qquad (2)$$

$$\begin{aligned} \mathrm{Hg} + \mathrm{XY} &\rightarrow \mathrm{HgX} + \mathrm{Y} \qquad (3)\\ &\rightarrow \mathrm{HgY} + \mathrm{X} \end{aligned}$$

for X = {Cl, Br} and Y = {Cl, Br, O}, where the most likely identities of XY in reaction 3 are the ClO and BrO radicals. Even basic thermochemical knowledge of these reactions, however, is relatively scarce. For instance, the mercury halides, HgCl and HgBr, are fairly well characterized experimentally, however their heats of formation are known to only a few kcal/mol. The experimental dissociation energy of the HgO molecule has recently been proposed by high level ab initio calculations to be in error by as much as 50 kcal/mol.[5] Among the possible HgXY species, $HgCl_2$ and $HgBr_2$ have been the subject of several experimental and theoretical studies, but their heats of formation are also only known to within a few kilocalories per mole. Only the fundamental vibrational frequencies of HgBrCl have been measured, and neither HgClO nor HgBrO has been observed by experiment. None of the species in this work involving Hg have been studied by high-resolution spectroscopy.

In the present work, the enthalpies of reactions 2 and 3 given above are calculated using accurate ab initio electronic structure methods. Sequences of correlation consistent basis sets are used in conjunction with highly correlated coupled cluster wave functions. After extrapolation to the complete basis set limit, additional corrections for zero-point vibrations, core−valence correlation, scalar relativity, pseudopotential errors, and spin−orbit effects are accurately included. A similar approach has been used for ab initio thermochemical investigations of a wide range of species with very high accuracy (cf., refs 6−10). In this work the final enthalpies of reaction, as well as enthalpies of formation for the HgXY complexes, are believed to be accurate to about ±1 kcal/mol and in nearly all cases should be significantly more reliable than the current experimental values. The details of the calculations are described in section II, while the results and summary are presented in sections III and IV, respectively.

II. Methodology

All ab initio electronic structure calculations were carried out using the MOLPRO suite of programs.[11] For the geometry optimizations the total energies of the molecules were obtained with the coupled cluster singles and doubles method with a perturbative correction for connected triple excitations, CCSD(T).[12] For all open-shell species the ROHF/UCCSD(T) method[13−15] was employed. If not otherwise mentioned, the excitations from the core orbitals were dropped from the correlation scheme, and only the O(2s2p), Cl(3s3p), Br(4s4p), and Hg(5d6s) electrons

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were correlated (frozen core approximation). Full symmetry equivalencing was always imposed on the HF orbitals.

The oxygen basis sets corresponded to the aug-cc-pV*n*Z sets, i.e., the standard correlation consistent cc-pV*n*Z basis sets[16] augmented with additional diffuse functions.[17] The new aug-cc-pV(n+d)Z basis sets were used for the chlorine atom. These are the standard aug-cc-pV*n*Z basis sets[18] with modified *d*-shells that contain additional tight exponents.[19] Small-core relativistic effective core potentials (RECP) were used for both mercury and bromine. The Hg RECP was that of Häussermann et al.[20] and included 60 electrons in the core. The Br RECP corresponded to a newly developed small core RECP[21] analogous to those recently reported for Ga−Se by Metz et al.[22] The remaining Hg ($5s^25p^65d^{10}6s^2$) and Br ($3s^23p^63d^{10}4s^24p^5$) electrons were treated with new correlation consistent basis sets denoted as aug-cc-pV*n*Z-PP. The Hg basis sets, which have recently been described in detail with benchmark calculations on HgH^+ and Hg_2,[23] consisted of contracted [4s4p3d1f], [6s6p5d2f1g], [7s7p6d3f2g1h], and [8s8p7d4f3g2h1i] sets for cc-pVDZ-PP, cc-pVTZ-PP, cc-pVQZ-PP, and cc-pV5Z-PP, respectively. The augmenting diffuse functions for Hg were obtained as even-tempered extensions of each angular momentum. In the case of Br, these basis sets will be reported separately with the other post-*d* group 16−18 elements in conjunction with the new RECP parameters.[21] Briefly, they consisted of contracted [4s3p2d], [5s4p3d1f], [6s5p4d2f1g], and [7s6p5d3f2g1h] sets for cc-pVDZ-PP through cc-pV5Z-PP, respectively. The usual shells of diffuse functions[17] were obtained by optimizations on the negative ion. Small molecule CCSD(T) benchmark calculations with these RECPs and basis sets[21] have demonstrated very small pseudopotential errors of about 0.002 Å and a few tenths of a kcal/mol in dissociation energies. In the remainder of this paper, the basis sets mentioned above will be denoted as AV*n*Z. Overall, basis sets with $n = 2$ (D), 3 (T), 4 (Q), and 5 were employed in our calculations. To calibrate the errors due to the pseudopotential approximation (see below), all-electron calculations were also carried out for all the species of this work using the Douglas−Kroll−Hess (DK) Hamiltonian.[24,25] The basis sets used in these calculations corresponded to the standard aug-cc-pVQZ basis sets recontracted in atomic DK−HF calculations for O, Cl, and Br. An aug-cc-pVQZ-DK basis set on Hg has been described previously[23] and consisted of a contracted [12s11p9d5f3g2h] set.

Complete basis set (CBS) limits of the total energies were obtained using both the 3-point mixed exponential/Gaussian extrapolation formula[6,26]

$$E(n) = E_{\mathrm{CBS}} + Be^{-(\mathrm{n}-1)} + Ce^{-(n-1)^2} \tag{1}$$

with $n = 3-5$ (CBS1) and the 2-point extrapolation formula[27,28]

$$E(n) = E_{\mathrm{CBS}} + B/n^3 \tag{2}$$

where $n = 4$ and 5 (CBS2). The final CBS limit total energies were obtained by averaging CBS1 and CBS2.

The near-equilibrium potential energy surfaces of the molecules involved in this study were obtained by fitting grids of energies to polynomials in simple displacement coordinates. The spectroscopic constants of the diatomic molecules were determined via the usual Dunham analysis.[29] The equilibrium distances, harmonic vibrational frequencies, and zero-point energies of the triatomics were obtained using the surfit program.[30] Extended details on these surfaces, as well as the resulting spectroscopic properties, will be reported elsewhere.[31]

Additive corrections to the frozen-core, CCSD(T)/CBS energetics were included for core−valence correlation (ΔE_{CV}), scalar relativistic effects (ΔE_{SR}), pseudopotential errors (ΔE_{PP}), and spin−orbit coupling (ΔE_{SO}). All of these corrections were obtained from singlepoint calculations at the CCSD(T)/CBS2 equilibrium geometries. The core−valence correlation correction, ΔE_{CV}, was determined as the difference in the CCSD(T) energies in calculations where excitations from all occupied orbitals were allowed and those where the frozen core approximation was employed. Both of these calculations were carried out with an aug-cc-pwCVQZ basis set[32] on oxygen, an aug-cc-pwCVQZ set on chlorine, aug-cc-pwCVQZ-PP on bromine, and cc-pwCVQZ-PP on mercury. These basis sets all contained additional tight functions in each angular momentum and were optimized explicitly for core−valence correlation effects.

The scalar relativistic corrections to the total energy, ΔE_{SR}, were initially obtained as a sum of the expectation values of the 1-electron Darwin and mass−velocity (MVD) terms in the Breit−Pauli Hamiltonian[33] calculated with the single reference configuration interaction singles and doubles (CISD) method and completely uncontracted AVTZ basis sets. This correction was nonzero for all species except those that consisted of only Hg and Br. In these latter cases the scalar relativistic contributions to the total energy were assumed to be already included in the RECP of these atoms. Closely related to ΔE_{SR} is the estimation of the errors associated with the pseudopotential approximation, ΔE_{PP}, where RECPs were used. This was obtained by carrying out all-electron CCSD(T)/aug-cc-pVQZ-DK calculations (frozen core approximation) on all of the species of this work. The corrections to the enthalpies were then calculated as the difference between the DK enthalpies and the enthalpies obtained from PP-based calculations (PPs on Hg and Br only) with the AVQZ basis sets. For all but the Hg + Br_2 reaction, these latter enthalpies also included ΔE_{SR}. Hence the final reaction enthalpies (and heats of formation) effectively include scalar relativistic corrections at the all-electron CCSD(T)/aug-cc-pVQZ-DK level of theory, since, in addition to PP errors, inaccuracies in ΔE_{SR} are also subsequently removed in ΔE_{PP}.

Last, the spin−orbit corrections, ΔE_{SO}, to both the atomic and molecular energies were found within the state-interacting approach; i.e., spin−orbit eigenstates were obtained by diagonalizing $H_{\mathrm{el}} + H_{\mathrm{SO}}$ in a basis of pure Λ−S electronic states. The spin−orbit matrix elements were calculated at the internally contracted MRCI level of theory[34] with use of spin−orbit pseudopotentials. The Hg 5d electrons were not correlated in these calculations. The basis sets corresponded to aug-cc-pVTZ-PP for both Hg and Br. Relativistic pseudopotentials were also applied on both O[35] and Cl[36,37] in order to employ these effective spin−orbit operators. The basis sets for the s- and p-shells of the aug-cc-pVTZ sets on O and Cl were recontracted in the presence of the RECPs. The orbitals used in the MRCI calculations were obtained using the state-averaged CASSCF method. All of the electronic states that correlated to the sum of Hg(^1S_g), Br(^2P_u), Cl(^2P_u), and O(^3P_g) atomic states were taken into account in the construction of $H_{\mathrm{el}} + H_{\mathrm{SO}}$. In the case of HgO, the O(^1D) asymptote was also included. The diagonal elements of $H_{\mathrm{el}} + H_{\mathrm{SO}}$ were replaced by the MRCI+Q energies, which included the multireference Davidson correction[38−40] for an approximate treatment of the effects of higher excitations. For the atoms, the errors using this treatment with respect to the experimental values (lowest spin−orbit level relative to the

TABLE 1: CCSD(T) Total Energies (au) and Equilibrium Distances (Å)

species		AVQZ	AV5Z	CBS1	CBS2	expt
$X^1\Sigma_g^+$ Cl_2	E_{min}	−919.48334	−919.49612	−919.50354	−919.50954	
	r_e	1.9967	1.9926	1.9902	1.9883	1.9880[f]
$X^1\Sigma_g^+$ Br_2	E_{min}	−831.41659	−831.42829	−831.43509	−831.44057	
	r_e	2.2964	2.2922	2.2897	2.2878	2.2810[a]
$X^1\Sigma^+$ BrCl	E_{min}	−875.45040	−875.46259	−875.46968	−875.47540	
	r_e	2.1476	2.1431	2.1405	2.1384	2.1370[b]
$X^2\Pi$ ClO	E_{min}	−534.79088	−534.80338	−534.81065	−534.81652	
	r_e	1.5737	1.5701	1.5681	1.5664	1.5696[e]
$X^2\Pi$ BrO	E_{min}	−490.75351	−490.76529	−490.77214	−490.77766	
	r_e	1.7250	1.7220	1.7203	1.7189	1.7173[c]
$X^2\Sigma^+$ HgCl	E_{min}	−612.75828	−612.77735	−612.78844	−612.79736	
	r_e	2.3870	2.3824	2.3798	2.3777	
$X^2\Sigma^+$ HgBr	E_{min}	−568.72276	−568.74133	−568.75215	−568.76083	
	r_e	2.5339	2.5298	2.5275	2.5256	
$X^1\Sigma^+$ HgO	E_{min}	−228.02436	−228.04352	−228.05467	−228.06361	
	r_e	1.9145	1.9124	1.9111	1.9101	
$X^1\Sigma_g^+ HgCl_2$	E_{min}	−1072.58646	−1072.61245	−1072.62757	−1072.63973	
	r_e	2.2549	2.2517	2.2498	2.2483	2.252(5)[g]
$X^1\Sigma_g^+ HgBr_2$	E_{min}	−984.50918	−984.53409	−984.54859	−984.56024	
	r_e	2.3897	2.3867	2.3849	2.3835	2.378(5)[d]
$X^1\Sigma^+$ HgBrCl	E_{min}	−1028.54778	−1028.57323	−1028.58803	−1028.59994	
	r_e(HgBr)	2.3805	2.3775	2.3758	2.3744	
	r_e(HgCl)	2.2643	2.2609	2.2590	2.2575	
$X^2\Pi$ HgClO	E_{min}	−687.849686	−687.87519	−687.89002	−687.90195	
	r_e(HgCl)	2.2488	2.2457	2.2440	2.2426	
	r_e(HgO)	1.9672	1.9652	1.9641	1.9632	
$X^2\Pi$ HgBrO	E_{min}	−643.81044	−643.83541	−643.84995	−643.86162	
	r_e(HgBr)	2.3752	2.3724	2.3708	2.3696	
	r_e(HgO)	1.9767	1.9747	1.9735	1.9726	

[a] Reference 62. [b] Reference 63, $r_e = 2.13605$ Å in ref 64. [c] Average of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ values from ref 65. [d] R_α structure from ref 45. [e] Average of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ values from ref 66. [f] Reference 67. [g] R_g structure from ref 46.

j-averaged energy) of Moore[41] were just −0.30, 0.02, and 0.02 kcal/mol for Br, Cl, and O, respectively.

III. Results and Discussion

The CCSD(T) total energies and equilibrium distances of the molecules obtained with the AVQZ and AV5Z basis sets are shown in Table 1, together with their respective CBS limits and the geometries available from experimental studies. The energy extrapolation to the CBS limit results in a shortening of the distances compared to the CCSD(T)/AV5Z ones. The equilibrium bond lengths determined from energies extrapolated with either CBS eq 1 or 2 differ by only 0.001−0.002 Å, and in general nearly all of the resulting r_e values are slightly longer than the experimental ones. One should, however, take into account that the effects of core−valence correlation and relativity have been neglected in the geometry optimizations of the present work. In particular, the inclusion of core−valence effects is expected to further decrease the bond lengths in most of these molecules. For example, the core−valence correlation contribution to the r_e of HgO has been calculated to be −0.009 Å,[5] while the bond distances in $HgCl_2$ and $HgBr_2$ were shortened by 0.006 and 0.009 Å, respectively.[31] It should be noted that the equilibrium geometries of HgBrCl, HgBrO, and HgClO shown in Table 1 are the first reported for these species.

As observed in Table 1, the calculated diatomic (Cl_2, Br_2, BrCl, ClO, and BrO) equilibrium distances are in excellent agreement with those obtained in spectroscopic studies. All of the HgXY insertion complexes (X = Br, Cl; Y = Br, Cl, O) are calculated to have linear equilibrium structures with Hg as the central atom. The Hg−Br bond lengths in the symmetric $HgBr_2$ molecule have been measured in several electron diffraction (ED) experiments[42−45] and lie in quite a wide range, 2.38−2.44 Å. Our CCSD(T)/CBS calculations yield a value of r_e(Hg−Br) = 2.384 Å, which is in very good agreement with the results of the ED study of Deyanov et al., $r_\alpha = 2.378 \pm 0.005$ Å.[45] Similar results were obtained for $HgCl_2$, where our CCSD(T)/CBS value for r_e, 2.249 Å, is consistent with the ED result of Kashiwabara et al.[46] (2.252 ± 0.005 Å). In both cases our calculated equilibrium bond lengths are shorter by 0.02−0.04 Å than previous ab initio studies, which all employed smaller basis sets and less sophisticated electron correlation methods (cf., refs 47−52 and references therein).

To our knowledge, reliable equilibrium geometries derived from experiment have not been published for the diatomics HgO, HgBr, and HgCl, as well as the HgBrCl, HgClO, and HgBrO molecules. The reader is referred to ref 5 for a detailed discussion of HgO. Equilibrium bond lengths of 2.62 and 2.42 Å for the electronic ground states of HgBr and HgCl, respectively, have been estimated in spectroscopic studies[53−55] and were based in part on the values of r_e(HgBr) = 2.61 Å and r_e(HgCl) = 2.41 Å determined in earlier ab initio CI calculations by Wadt.[56] According to our results, however, shown in Table 1, the equilibrium distances for both of these molecules are shorter by as much as ~0.1 Å; i.e., r_e(HgBr) = 2.527 Å and r_e(HgCl) = 2.379 Å at the CCSD(T)/CBS level of theory.

The CCSD(T) harmonic frequencies of all the species considered in this work are given in Table 2 along with the available experimental harmonic frequencies for the diatomics and fundamental frequencies of $HgCl_2$, $HgBr_2$, and HgBrCl. The CBS extrapolation formulas 1 and 2 yield nearly the same results for the stretching frequencies. The full sets of vibrational frequencies were calculated only at the CCSD(T)/AVQZ level. In general, the CCSD(T)/AVQZ frequencies are very close to both the CBS limit values and the experimental data, with the exception of HgCl where the CCSD(T)/AVQZ harmonic frequency is lower by 15 cm^{-1} than the experimental value. The remaining errors in the calculated harmonic frequencies, which are mainly due to the neglect of residual relativity and

TABLE 2: CCSD(T) Harmonic Vibrational Frequencies (cm^{-1})

species		AVQZ	AV5Z	CBS1	CBS2	expt
Cl_2		556.3	561.1	563.9	566.2	559.71[j]
Br_2		323.7	326.1	327.4	328.4	325.31[a]
ClO		854.3	858.6	861.2	863.3	853.64[i]
BrO		726.0	729.6	731.8	733.5	725.42[c]
BrCl		442.4	446.0	448.2	449.9	444.26[b]
HgBr		183.2	184.4	185.0	185.6	188.25[d]
HgCl		285.4	287.7	289.1	290.2	298.97[e]
HgO		596.7	599.2	600.6	601.8	676[f]
$HgCl_2$	(Σ_g)	360.3	362.3	363.5	364.4	355[g], 358,[o] 365,[m] 366[n]
	(Π_u)	101.6				100[k]
	(Σ_u)	414.6	416.4	417.5	418.3	413[h]
$HgBr_2$	(Σ_g)	222.5	223.2	223.6	224.0	220,[g] 218,[l] 229,[m] 222[o]
	(Π_u)	68.1				68[k]
	(Σ_u)	293.2	293.9	294.3	294.7	293[h]
HgBrCl	(HgBr)	255.6	256.4	256.9	257.3	253[l]
	(bend)	85.1				83[k]
	(HgCl)	387.9	389.7	390.7	391.6	385[l]
HgClO	(HgCl)	386.6	388.2	389.1	389.8	
	(bend)	138.1				
	(HgO)	592.2	594.4	595.6	596.6	
HgBrO	(HgBr)	262.7	263.2	263.6	263.9	
	(bend)	122.5				
	(HgO)	580.2	582.3	583.8	584.8	

[a] Reference 62. [b] Reference 64. [c] Average of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ values from ref 65. [d] Reference 53. [e] Reference 54. [f] Reference 68. [g] Reference 69. [h] Reference 70. [i] Average of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ values from ref 66. [j] Reference 67. [k] Reference 71. [l] Reference 72. [m] Reference 73. [n] Reference 74. [o] Reference 75.

core−valence correlation effects, should result in only very small (no more than 0.1 kcal/mol) errors in the calculated zero-point energies. The near-equilibrium potential function of HgO has been previously shown[5] to be strongly affected by spin−orbit effects, and the zero-point energy for this species has been taken from ref 5 for the thermochemical analysis below. A more detailed analysis of the structure and vibrational spectra of the HgXY (X = Br, Cl; Y = Cl, Br, O) species will be presented in a separate publication.[31]

The calculated enthalpies of reaction for both the abstraction and insertion reactions of Hg + XY (X = Br, Cl; Y = Br, Cl, O) are shown in Table 3. All of the abstraction reactions are endothermic by 30−60 kcal/mol. On the other hand, the insertion complexes are lower than reactants by 20−50 kcal/mol. The CBS limit ΔE_e values were calculated using total energies obtained by averaging the results of CBS extrapolation formulas 1 and 2. The CBS values differ from those calculated with the largest basis sets by only 0.1−0.5 kcal/mol. The zero-point energy corrections were evaluated using the CCSD(T)/AVQZ harmonic frequencies. The other corrections to the CCSD(T)/CBS values, i.e., ΔE_{CV}, ΔE_{SR}, ΔE_{PP}, and ΔE_{SO}, are generally small but have nonnegligible cumulative effects. The errors due to the pseudopotential approximation, which can mainly be attributed to the PP employed on Hg (compare, for instance, ΔE_{PP} for Hg + Cl_2 vs Hg + Br_2), are larger than expected in many cases, i.e., 0.5−1.6 kcal/mol. In every case this latter correction brings the calculated reaction enthalpies closer to the middle of the experimental ranges where these are available. The largest contributions from ΔE_{SO} are observed among the reactions involving Br atom, which is mostly due to its large $^2P_{1/2}$−$^2P_{3/2}$ zero-field splitting. As shown in Table 3, the experimental enthalpies of reaction have large uncertainties due in part to the large experimental uncertainties in the heats of formation of HgCl and HgBr. The reaction enthalpies calculated in this work are all within the experimental uncertainties (see ref 5 for a discussion of the reactions producing HgO) and are expected to have smaller errors (~1 kcal/mol). Similar calculations that were recently reported[10] for several small halogenated molecules yielded bond enthalpies for Cl_2, Br_2, and BrCl that agreed with experiment to within a few tenths of a kcal/mol. Thus, the current calculated results are expected to be the most accurate available for these reactions. In addition, using our calculated enthalpies of reaction for Hg + BrX and Hg + ClX (X = Br, Cl, O) and accurate experimental heats of formation (Hg, Br_2, BrCl, BrO, ClO, Br, Cl, and O, see below), the heats of formation of HgBr and HgCl can be refined compared to the existing experimental values to be $\Delta H_f(0K) = 28.4 \pm 1.2$ kcal/mol for HgBr and $\Delta H_f(0K) = 21.8 \pm 1.1$ kcal/mol for HgCl (the values are obtained by averaging the results for three individual reactions in each case). These can be compared to the JANAF values[57] of 27.6 ± 9.1 and 19.7 ± 2.3 kcal/mol for HgBr and HgCl, respectively.

The calculated 0 K heats of formation of the insertion complexes, together with their dissociation energies, are collected in Table 4. The former quantities were predicted using accurate experimental $\Delta H_f(0K)$ values for the other relevant species [$\Delta H_f(0K) = 15.42 \pm 0.01$ kcal/mol for Hg(g), 28.18 ± 0.01 kcal/mol for Br(g), 28.590 ± 0.001 kcal/mol for Cl(g), 58.98 ± 0.02 kcal/mol for O(g), and 10.92 ± 0.03 kcal/mol for Br_2(g) from JANAF,[57] 5.24 ± 0.02 kcal/mol for BrCl(g) using Tellinghuisen's[58] D_0(BrCl), 24.14 ± 0.03 kcal/mol for ClO(g) using the D_0(ClO) of Coxon and Ramsay,[59] and $\Delta H_f(0K) = 31.96 \pm 0.41$ kcal/mol for BrO from Wilmouth et al.[60]]. Our calculated enthalpy of formation for $HgBr_2$, −16.3 kcal/mol, is

TABLE 3: Calculated Energetic Contributions[a] and Resulting (0 K) Enthalpies of Reaction, ΔH_r (kcal/mol)

	ΔE_e(5Z)	ΔE_e(CBS)	ΔE_{ZPE}	ΔE_{CV}	ΔE_{SR}	ΔE_{PP}	ΔE_{SO}	ΔH_r	expt[b]
Hg + Br_2 → HgBr + Br	33.19	33.62	−0.20	0.68		−0.53	−3.01	30.6	29.44 ± 9.13
→ $HgBr_2$	−41.64	−41.89	0.47	0.00		−1.31	0.31	−42.4	−42.42 ± 2.05
Hg + Cl_2 → HgCl +Cl	35.73	36.27	−0.39	0.73	0.05	−0.70	−0.84	35.1	32.89 ± 2.29
→ $HgCl_2$	−48.25	−48.49	0.59	0.31	0.30	−1.38	0.02	−48.7	−49.44 ± 1.52
Hg + BrCl → HgBr + Cl	37.30	37.79	−0.37	0.49	0.02	−0.67	−0.77	36.5	35.49 ± 9.39
→ HgCl + Br	32.12	32.55	−0.22	0.80	0.17	−0.71	−2.94	29.7	27.21 ± 2.62
→ HgBrCl	−44.67	−44.94	0.53	0.10	0.25	−1.46	0.24	−45.3	
Hg + BrO → HgBr + O	39.40	39.64	−0.78	0.26	0.09	−0.76	1.00	39.5	39.21 ± 9.52
→ HgO + Br	55.04	55.22	−0.40[c]	0.04	0.12	−0.56	−4.27	50.2	−8.08 ± 15.49
→ HgBrO	−19.25	−19.49	0.52	−0.40	0.22	−1.55	0.55	−20.2	
Hg + ClO → HgCl +O	40.71	41.07	−0.81	0.76	−0.01	−0.68	0.25	40.6	39.08 ± 2.83
→ HgO + Cl	61.52	61.88	−0.58[c]	0.22	−0.12	−0.44	−2.85	58.1	0.07 ± 15.57
→ HgClO	−20.31	−20.44	0.38	0.02	0.14	−1.36	−0.35	−21.6	

[a] ΔE_e = CCSD(T) electronic energy difference, ΔE_{ZPE} = zero-point energy contribution, ΔE_{CV} = core−valence correlation contribution, ΔE_{SR} = scalar relativity correction (MVD), ΔE_{PP} = correction for pseudopotential approximation, ΔE_{SO} = spin−orbit coupling contribution. See text. [b] Reference 57. [c] ZPE contributions for HgO were taken from ref 5.

TABLE 4: Calculated Dissociation Energies and (0 K) Heats of Formation for HgXY Species (in kcal/mol)[a]

XHgY	D_0(XHg + Y)	D_0(X + HgY)	ΔH_f
BrHgBr	73.0		−16.3 (−16.08 ± 2.01)
ClHgCl	83.8		−33.2 (−34.01 ± 1.51)
BrHgCl	81.8	75.0	−24.6
BrHgO	59.7	70.4	+27.2
ClHgO	62.2	79.7	+17.9

[a] Experimental values are in parentheses.[57]

in excellent agreement with its accepted experimental value (−16.08 ± 2.01),[57] and suggests the experimental uncertainty is fairly conservative. The calculated ΔH_f(0K) for $HgCl_2$, −33.2 kcal/mol, is near the lower end of the experimental range (−34.01 ± 1.51). The small basis set MP2 calculations of Barone[51] yielded heats of formation for $HgBr_2$ and $HgCl_2$ that were somewhat more negative than the present results. This same level of theory yielded dissociation energies of 71.2 and 82.3 kcal/mol for $HgBr_2$ and $HgCl_2$, respectively, which are smaller by about 1−2 kcal/mol than the values shown in Table 4. All of the complexes in this work are predicted to be strongly bound with respect to loss of a halogen atom. However, due to the relatively high barrier between the Hg + XY reactants and the insertion complexes,[61] the reactions HgX + Y (X = Br, Cl; Y = Br, Cl, O), which occur without a barrier,[61] are expected to be the dominant formation and loss channels for these species.

IV. Summary

The thermochemistry of the reactions of Hg atom with several small halogenated compounds has been accurately calculated using highly correlated coupled cluster methods with systematic treatments of basis set truncation errors, scalar and spin−orbit relativistic effects, pseudopotential errors, and core−valence correlation. The resulting 0 K reaction enthalpies, as well as the heats of formation of the complexes $HgCl_2$, $HgBr_2$, HgBrCl, HgClO, and HgBrO, are estimated to be accurate to within 1 kcal/mol, which is generally much more accurate than the existing experimental values. All of the abstraction reactions are endothermic by 30−60 kcal/mol. The insertion complexes are all strongly bound, however, and probably represent important reactive gaseous mercury (RGM) compounds in the troposphere. Calculations to accurately determine their atmospheric lifetime using large-scale potential energy surfaces of similar quality as reported in this work are currently in progress.

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