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Ab Initio Thermochemistry Involving Heavy Atoms: An Investigation of the Reactions Hg + IX (X = I, Br, Cl, O)

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Accurate 0 K enthalpies have been calculated for reactions of mercury with a series of small iodine-containing molecules (I_2, IBr, ICl, and IO). The calculations have been carried out with the coupled cluster singles and doubles method with a perturbative correction for connected triple excitations [CCSD(T)] using sequences of correlation consistent basis sets and accurate relativistic pseudopotentials. Corrections have been included to account for core-valence correlation, spin−orbit coupling, scalar relativity, and the Lamb shift. In a few cases coupled cluster calculations with iterative triple (CCSDT) and quadruple (CCSDTQ) excitations have been carried out to estimate the effects of higher order electron correlation. The pseudopotential calculations have also been compared to all electron calculations using second- and third-order Douglas−Kroll−Hess Hamiltonians. In addition to the reaction enthalpies, heats of formation, bond lengths, and harmonic vibrational frequencies have been calculated for the stable triatomic products HgI_2, HgIBr, HgICl, and HgIO. Accurate dissociation energies, equilibrium bond lengths, and harmonic vibrational frequencies have also been calculated for each of the diatomic molecules involved in this study (HgI, HgBr, HgCl, HgO, I_2, IBr, ICl, and IO). The reported enthalpies are expected to have accuracies of 1 kcal/mol or better.

Introduction

In the atmosphere, mercury exists predominately in the gas phase and zero oxidation state. Mercury in this form is fairly inert, giving it long atmospheric residence times that are on the order of 1−2 yr. This allows mercury to be transported far from its anthropogenic and natural sources and gives mercury a nearly uniform background concentration across the globe.[1] Episodic depletions of this background atmospheric mercury concentration in the Arctic troposphere during polar sunrise were first observed by Schroeder et al. at Alert, NT (83° N, 63° W).[2] Since those first observations, mercury depletion events (MDEs) have been observed elsewhere in the Arctic[3−5] as well as the Antarctic.[6] Similar tropospheric ozone depletion events have been observed to be highly correlated with the MDEs.[2−6] Reactions of ozone with reactive photochemically produced halogen species are known to be responsible for the ozone depletion events,[7−12] and it has been proposed that these halogen species are also responsible for the depletions of tropospheric mercury. The proposed mechanism of the mercury depletions is that the gas-phase zero-valent mercury undergoes oxidizing reactions with the photochemically produced halogen species to generate some form of reactive gaseous mercury, which is then deposited onto the snowpack. A recent study by Tarasick and Bottenheim[13] has shown that the occurrence of ozone depletion events in the Arctic have been increasing since the 1960s and blame this rise on increasing global temperatures. It is likely then that the frequency of mercury depletions has been rising as well. This increase has been suggested as a partial cause of the high concentrations of mercury in Arctic biota.[3,13]

When the MDEs were first observed, there was very little known about the gas phase thermochemistry and kinetics of the reactions between mercury and halogen species. Since then, several theoretical[14−17] and experimental[18,19] studies have been reported for reactions of mercury with bromine- and chlorine-containing species. Similar attention has not been given to the possible role of iodine in mercury depletion events. Goodsite et al.[17] reported density functional theory (DFT) calculations that included the molecules HgI and HgIBr as well as a rate constant for the recombination of Hg and I atoms using RRKM theory. Also, Calvert and Lindberg[20] performed an atmospheric modeling study of Arctic tropospheric mercury that included iodine chemistry. This and other modeling studies could benefit from an accurate characterization of the reactions of mercury with iodine-containing species that might be involved.

Before the observation of MDEs, the primary interest in gaseous mercury halides was in connection with laser applications. The UV absorption[21−24] and dissociation[25−30] of HgX_2 and the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions of HgX (X = Br, Cl, I)[31−40] have received a fair amount of attention. The infrared and Raman spectra of matrix-isolated[41−44] and gas-phase[45−47] HgIX (X = Br, Cl, I) have also been characterized. Additionally, HgI_2 has been the focus of crossed molecular beam experiments[48−50] and femtosecond transition-state spectroscopy that focused on its photodissociation.[51−54] There have also been a small number of theoretical investigations of HgI and HgI_2,[55−57] but these employed relatively small basis sets and modest levels of electron correlation.

Due to the relatively small body of work on mercury−iodine species, the goal of this work was to accurately compute the thermochemistry of several reactions that involve mercury and iodine that might be important in mercury depletion events. The specific reactions investigated were

$$\mathrm{Hg + IX} \rightarrow \begin{cases} \mathrm{HgX + 1} \\ \mathrm{HgI + X} \\ \mathrm{IHgX} \end{cases}$$

where X = O, Cl, Br, and I. Currently, the enthalpies of many of these reactions are not known accurately or are not known

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at all. In this work, highly correlated ab initio calculations have been carried out on the above reactions and the heats of formation of linear IHgX (X = O, Cl, Br, I). The present study included the calculation of full near-equilibrium potential energy surfaces for each of the above diatomic and triatomic molecules to determine not only their thermochemistry but also their spectroscopic properties. This paper will focus solely on the thermochemistry, while a future paper will address the structures and spectroscopy in more detail. Electron correlation was treated with the coupled cluster singles and doubles method with a perturbative treatment of connected triple excitations[58] [CCSD(T)] and series of correlation consistent basis sets that were used to extrapolate to the complete basis set (CBS) limit. Additionally, corrections for core-valence correlation, spin−orbit coupling, the Lamb shift, and scalar relativity were also included. A small number of coupled cluster calculations including iterative triple (CCSDT) and quadruple (CCSDTQ) excitations have also been carried out. The reported heats of reaction are expected to be the most accurate values available and have estimated uncertainties of 1 kcal/mol. Also, the bond lengths reported here for the molecules HgX and HgIX (X = O, Cl, Br, I) should be considered the most reliable to date.

Methodology

To account for the large scalar relativistic effects in the compounds under investigation, small-core energy consistent pseudopotentials of the Stuttgart/Köln type were used for Br,[59] I,[59] and Hg.[60] These pseudopotentials treat the valence and semicore electrons explicitly, and the inner core electrons are replaced by the pseudopotential. The explicitly treated electrons for Br (25 e$^-$), I (25 e$^-$), and Hg (20 e$^-$) are as follows: $3s^2 3p^6 3d^{10} 4s^2 4p^5$, $4s^2 4p^6 4d^{10} 5s^2 5p^5$, and $5s^2 5p^6 5d^{10} 6s^2$, respectively. Correlation consistent basis sets from double-ζ to quintuple-ζ quality have recently been developed for use with these pseudopotentials and are denoted cc-pVnZ-PP (n = D, T, Q, 5).[59,61] Augmented sets that include an extra diffuse function of each angular momentum type have also been used and are denoted aug-cc-pVnZ-PP.[59,61] The aug-cc-pV($n + d$)Z sets[62] were used for Cl, and the standard aug-cc-pVnZ sets[63] were used on oxygen. From this point forward the abbreviation aVnZ will be used to represent the above listed augmented sets for each atom. Most calculations in this study were performed with the CCSD(T) method[58] and have employed the frozen core approximation except where noted. For the open-shell molecules the calculations were performed at the ROHF/UCCSD(T)[64−66] level of theory, which uses restricted open-shell Hartree−Fock orbitals but allows for some spin-contamination in the coupled cluster calculations. Except where stated otherwise, all calculations were performed with the MOLPRO[67] suite of ab initio programs.

A grid of 74 points was calculated on the potential energy surface of each triatomic molecule (IHgI, IHgBr, IHgCl, and IHgO), and 7 points were calculated for each diatomic (HgI, HgBr, HgCl, HgO, I_2, IBr, ICl, and IO). The actual number of points that had to be explicitly calculated for the triatomic molecules was reduced by symmetry to 31 for IHgI and 50 for IHgX (X = Cl, Br, O). These grids of energies were computed for each species using all four basis sets in the series aVnZ (n = D, T, Q, 5), except that in the case of the triatomic molecules the aVQZ basis set was the largest used for nonlinear geometries. Several methods for estimating the CBS limit from calculations with a series of correlation consistent basis sets have been proposed in the literature. In this work two formulas were used to extrapolate the total energies to the CBS limit:

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

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

The best estimate of the CBS limit was taken to be the average of the limits determined from eqs 1[68,69] and 2.[70,71] The triatomic potential energy surfaces were fit with polynomials in internal displacement coordinates using the program SURFIT.[72] Equilibrium geometries and harmonic vibrational frequencies were determined from these fits. The diatomic curves were also fit with polynomials and the usual Dunham analysis[73] was used to calculate the equilibrium geometries and harmonic frequencies. Zero-point vibrational energies (ZPE) were calculated as ZPE = $1/2\sum\omega_e$. where the ω_e values are the harmonic vibrational frequencies. Due to the heavy atoms involved, the anharmonic frequencies differed from the harmonic ones by only a few wavenumbers. Thus, the anharmonic ZPE corrections always differ from the harmonic values by less than 0.01 kcal/mol for all of the reactions in this study.

Several corrections were then applied to the valence electrons correlated CCSD(T)/CBS energies: core-valence correlation (ΔE_{CV}), spin−orbit coupling (ΔE_{SO}), scalar relativity (ΔE_{SR}), and the Lamb shift (ΔE_{Lamb}). The core-valence, spin−orbit, and scalar relativistic corrections were computed for each symmetry unique point on the potential surfaces, and the corrections used in the thermochemistry calculations were defined relative to their respective minimum geometries. In the core-valence calculations aug-cc-pwCVTZ-PP[61,74] basis sets were used on Br, I, and Hg, and the aug-cc-pwCVTZ[75] sets were used for Cl and O. Two separate calculations were carried out using the core-valence basis sets to determine this correction, one calculation with the standard frozen core and a second in which both the core and valence electrons were correlated. The core-valence correction was then taken as the difference between these two results. Note, however, that the Cl 1s electrons were kept frozen in all cases.

The Hg 4f electrons are replaced by the pseudopotential, but energetically lie above the Hg 5s in all-electron calculations. To account for effects on the enthalpies due to the correlation of the Hg 4f electrons, all-electron CCSD(T) calculations have been performed with the second-order Douglas−Kroll−Hess Hamiltonian (DK2) [76,77] as implemented in MOLPRO. For I, Br, and Hg the basis sets used in these calculations were of augmented triple-ζ quality and corresponded to newly developed all-electron core-valence correlation consistent basis sets where the exponents and contraction coefficients were optimized using the DK2 Hamiltonian and are denoted cc-pwCVTZ-DK[61,74] (aug-cc-pwCVTZ-DK). Standard aug-cc-pwCVTZ basis sets recontracted in atomic DK2 calculations[78] were employed for Cl and O. Three all-electron CCSD(T) calculations were performed with these basis sets at the CCSD(T)/CBS+CV+SO equilibrium geometries (CV refers to the core-valence correction described above and SO to the spin−orbit correction described below). In the first calculation only the valence electrons were correlated, in the second calculation the valence electrons together with the outer core electrons (Hg: 5s5p, I: 4s4p4d, Br: 3s3p3d, Cl: 2s2p, O: 1s) were correlated (where the 5s orbitals were rotated if needed above the 4f orbitals), and in the third the Hg 4f electrons were included in the correlation treatment. The contribution of the Hg 4f electrons to the core-valence energy was calculated as the difference between the second and third calculations and is denoted $\Delta E_{\mathrm{CV-f}}$.

A third correction applied to the CBS limit energy differences was to account for spin−orbit coupling. The one-electron spin−orbit operators used were those accompanying the pseudopotentials described above for Br, I, and Hg. For the spin−orbit calculations, relativistic pseudopotentials were also used for O[79] and Cl[80,81] and were again of the Stuttgart/Köln type. In the oxygen case the $1s^2$ electrons are replaced by the pseudopotential, and in the case of chlorine the $1s^22s^22p^6$ electrons are replaced. The basis sets used with the O and Cl pseudopotentials were the standard aug-cc-pVTZ basis sets (aug-cc-pV(T+*d*)Z for Cl), but they were recontracted in the presence of the pseudopotentials. The basis sets for Br, I, and Hg corresponded to the standard aug-cc-pVTZ-PP. The spin−orbit calculations were carried out using the multireference configuration interaction with single excitations method (MRCIS) using standard full-valence complete active spaces. The spin−orbit CI[82] code in the COLUMBUS[83] suite of ab initio programs was used in these cases. Two calculations were again carried out for each geometry, one corresponding to a standard MRCIS without spin−orbit coupling and the second was a spin−orbit-MRCIS (SO-MRCIS) that mixed all possible singlets and triplets (or doublets and quartets) via the spin−orbit operator. The orbitals used in each of these two calculations were natural orbitals obtained from configuration interaction singles and doubles (CISD) calculations performed with MOLPRO. The spin−orbit correction at each point was then defined as the difference between the SO-MRCIS energy and the MRCIS energy. The accuracy of the spin−orbit correction calculated in this manner is quite reasonable. For example, the zero-field splittings of the I, Br, and Cl atoms were calculated to be 7157, 3445, and 912 cm^{-1}, respectively, which can be compared to experimental values[84] of 7603, 3685, and 912 cm^{-1}. Therefore, the calculated differences between the *j*-averaged levels and $j = 3/2$ levels are in error with respect to experiment by −0.42 kcal/mol, −0.23 and 0.03 kcal/mol for I, Br, and Cl, respectively. Further improvement would presumably require the correlation of the outer-core electrons in the SO−CI calculations.

The spin−orbit correction for the reaction Hg + IO → HgO + I could not be treated in the same manner. If spin−orbit coupling is not included, HgO has two low-lying excited states[85] that are nearly isoenergetic, $^1\Sigma^+$ and $^3\Pi$. When spin−orbit coupling is included, the ground state is described as an $\Omega = 0^+$ state that is a mixture of the 0^+ components of the $^3\Pi$ and $^1\Sigma^+$ states. To describe the relative energetics of these states in even a qualitatively correct manner, accurate inclusion of both electron correlation and basis set effects are required. The MRCIS/aVTZ level of theory is not sufficient. These challenges were described in detail in a previous paper.[85] Therefore, the SO correction for HgO was determined using the interacting states approach in MOLPRO[86] in a similar procedure as our previous study[85] and will be discussed in detail in a future publication. Briefly, the diagonal elements of $H_{el} + H_{so}$ for several low-lying Λ-S states were computed with the internally contracted multireference configuration interaction with single and double excitations method[87,88] and included the multireference analogue of the Davidson correction[89−91] (icMRCI+Q). Correlation consistent basis sets of TZ-5Z quality were used, and energies were extrapolated to the CBS limit. A correction for core-valence correlation computed at the icMRCI+Q/aVTZ level was also included. All other diagonal matrix elements and all off-diagonal matrix elements of $H_{el} + H_{so}$ were computed at the icMRCI+Q/aVTZ level of theory. The states used to construct $H_{el} + H_{so}$ included all the singlets and triplets arising from Hg(^{1}S,^{3}P) + O(^{3}P,^{1}D,^{1}S) with the exception of the highest lying $^3\Sigma^-$ and $^1\Sigma^-$ states. The lowest energy $\Omega = 0^+$ state resulting from the diagonalization of $H_{el} + H_{so}$ was taken as the ground-state energy of HgO and is the energy used in the present thermochemical calculations. The ZPE and fundamental vibrational frequency of HgO was calculated for this $\Omega = 0^+$ state using the program LEVEL.[92]

The fourth correction, ΔE_{SR},was to account for scalar relativistic effects in the Cl and O atoms. Scalar relativistic effects for Br, I, and Hg were included in the parametrization of the pseudopotentials. Scalar relativistic corrections for molecules containing Cl and O atoms were determined by evaluating the expectation values of the mass-velocity plus Darwin terms of the Breit−Pauli Hamiltonian with the CISD method using completely uncontracted aVTZ basis sets.

It has recently been suggested that the Lamb shift, the leading quantum electrodynamic (QED) effect not included in the parametrization of the pseudopotentials, may be of chemical significance especially for molecules containing atoms as heavy as mercury.[93,94] To estimate the effects of the Lamb shift, we follow the procedure of Pyykkö and Zhao[95] involving local model potentials. The leading Lamb-shift contributions are the self-energy and vacuum polarization terms. The self-energy potential on each atom was simulated by a single Gaussian function whose coefficients and exponents were taken from Pyykkö and Zhao.[95] To simulate the vacuum polarization contribution for each atom a series of five Gaussian functions were fit to the parametrized representation of the vacuum polarization potential given by Pyykkö and Zhao.[95] The Lamb-shift correction was then determined from two all-electron CCSD(T)-DK2/aug-cc-pVTZ-DK calculations carried out at the equilibrium geometries; one calculation including the local potentials when computing the one-electron integrals and the other neglecting them.

One final correction was applied, but only in the determination of the dissociation energies of a few of the diatomic molecules. In particular there has been considerable disagreement in the literature about the heat of formation and dissociation energy of the IO molecule. To further refine our predictions for these quantities, additional single-point calculations were carried out at the CCSDT/aVTZ and CCSDTQ/aVDZ levels of theory using the NWChem[96,97] suite of ab initio programs. To obtain an estimate of the effect of iterative triples and quadruples on some of the other molecules in this study, CCSDT and CCSDTQ calculations were also carried out on the IBr and HgBr molecules. In the case of HgBr only the VDZ basis sets were used in the CCSDTQ calculations in order to reduce the computational requirements.

As part of this study, we were also interested in comparing reaction enthalpies computed with the pseudopotentials with enthalpies calculated with all electron Douglas−Kroll−Hess Hamiltonians of second (DK2) and third (DK3)[98] order. For I, Br, and Hg the basis sets used in these calculations corresponded to newly developed all-electron correlation consistent basis sets where the exponents and contraction coefficients were optimized using the DK2 Hamiltonian and are denoted cc-pV*n*Z-DK[59,99] (aug-cc-pV*n*Z-DK). Standard aV*n*Z basis sets recontracted in atomic DK2 calculations[78] were employed for the other atoms (aV(*n*+*d*)Z for Cl). For the DK2 enthalpies geometry optimizations using numerical gradients were carried out with the CCSD(T) method and the aug-cc-pV5Z-DK basis sets with MOLPRO. These were then compared to the CCSD(T)/aug-cc-pV5Z-PP + ΔE_{SR} enthalpies. By including ΔE_{SR} in this way we account for the neglect of scalar relativistic effects on Cl and O in the pseudopotential calculations.

For the DK3 enthalpies, calculations were carried out at the second-order Møller−Plesset perturbation theory (MP2) level with the GAMESS[100] suite of ab initio programs. cc-pV5Z-DK

TABLE 1: Equilibrium Bond Lengths (Å) and Harmonic Frequencies (cm^{-1})[a,b]

species		r_e	ω_e
$X^1\Sigma^+_{0+}$	I_2	2.6643	218.1
		2.6664[g]	*214.5*[g]
$X^1\Sigma^+_{0+}$	IBr	2.4673	272.6
		2.4690[h]	*268.9*[h]
$X^1\Sigma^+_{0+}$	ICl	2.3169	391.8
		2.3210[i]	*384.3*[i]
$X^2\Pi_{3/2}$	IO	1.8666	685.7
		1.8676[j]	*681.7*[j]
$X^2\Sigma^+_{1/2}$	HgI	2.7075	132.4
			125.4[l]
$X^2\Sigma^+_{1/2}$	HgBr	2.4976	192.7
			188.3[m]
$X^2\Sigma^+_{1/2}$	HgCl	2.3541	299.8
			299.0[n]
$\Omega = 0^+$	HgO	1.9184	231.0[c]

species		R_e (Hg-I)	R_e (Hg-X)	ω_e (Hg-I)[d]	ω_e (bend)[e]	ω_e (Hg-X)[f]
$X^1\Sigma^+_{g,0+}$	HgI_2	2.5460		163.7	53.7	240.5
		2.554[k]		*155,*[o] *158,*[p]	*63,*[r] *51,*[s]	*237.5*[q], *235*[k]
				163.5,[q] *156*[k]	*51*[k]	
$X^1\Sigma^+_{0+}$	HgIBr	2.5343	2.3785	188.0	62.2	278.1
				182,[o] *187.6*[q]	*66,*[r] *60*[s]	*266,*[o] *272.0*[q]
$X^1\Sigma^+_{0+}$	HgICl	2.5261	2.2558	206.2	79.5	388.4
				196,[o] *201.5*[q]	*83.5,*[r] *85,*[r] *74*[s]	*371,*[o] *378.0*[q]
$X^2\Pi_{3/2}$	HgIO	2.5214	1.9617	211.9	120.5	584.5

[a] Values are calculated at the CCSD(T)/CBS+CV+SO+SR level of theory. See text for explanation. [b] Experimental values in italics. [c] For HgO, this is the fundamental vibrational frequency and not the harmonic vibrational frequency. [d] For HgI_2 this is the Σ_g symmetric stretch. [e] CBS limits for bending frequencies use DZ-QZ basis sets. [f] For HgI_2 this is the Σ_u asymmetric stretch. [g] Ref 120. [h] Ref 121. [i] Ref 122. [j] Ref 123. [k] Ref 104 frequencies are harmonic. [l] Ref 36. [m] Ref 34. [n] Ref 35. [o] Ref 45. [p] Ref 46. [q] Ref 43. [r] Ref 42. [s] Ref 124.

basis sets were used in these calculations with the *h* and *i* angular momentum functions removed from the Hg basis set, and the *g* and *h* angular momentum functions removed from the basis sets of the other atoms. These truncations were employed since gamess can only handle up to *g*-type angular momentum functions. Only single-point calculations at the CCSD(T)/CBS+CV+SO equilibrium geometry were carried out. These enthalpies were then compared to (GAMESS) DK2 calculations using the same basis sets and at the same geometries. Direct comparison between the molpro pseudopotential results and the DK3 calculations in gamess were complicated by different implementations of the open-shell MP2 method in the two program packages.

It should be noted that the DK2 method in MOLPRO and GAMESS are of slightly different implementations. Some single-point calculations using DK2 in GAMESS and MOLPRO differed by a few mE_h, but there was virtually no difference when energy differences were considered. For example, the reaction enthalpies of $Hg + I_2 \rightarrow HgI_2$ and $Hg + IBr \rightarrow HgIBr$ calculated at the MP2-DK2 level of theory differed by 0.02 and 0.01 kcal/mol, respectively, depending on whether GAMESS or MOLPRO was used.

Results and Discussion

Table 1 shows the equilibrium bond lengths calculated at the CCSD(T)/CBS+CV+SO+SR (does not include correlation of the Hg 4f electrons) level of theory for the four triatomic and eight diatomic molecules involved in this study. In the four cases where experimental bond lengths are available for the diatomics (I_2, IBr, ICl, and IO), there is excellent agreement between the calculated and the experimental values. The RMS value of the difference between theory and experiment is just 0.0025 Å, and the maximum difference occurs for the ICl molecule and is just 0.0041 Å. To our knowledge, reliable experimental equilibrium geometries have not been reported for the diatomic molecules HgO, HgCl, HgBr, and HgI. A number of groups have reported previous DFT[17,57] and ab initio[15,16,31,101−103] calculations of the diatomic HgX (X = Cl, Br, I) bond lengths, but all involved smaller basis sets and lower levels of electron correlation than the present study. All four triatomic molecules have linear equilibrium geometries with Hg as the central atom. The only triatomic molecule for which an experimental bond length has been reported is HgI_2, and our calculated value of 2.546 Å is in reasonably good agreement with the experimental electron diffraction value[104] ($r_e = 2.554 \pm 0.003$ Å), being just 0.008 Å shorter. There have been a few previous theoretical calculations of the HgI_2 bond length[55−57] and one study involving the geometry of HgIBr,[17] but these only involved basis sets of DZ or TZ quality at the MP4,[55] MP2,[56] LDF,[57] and B3LYP[17] levels of theory. For the species without reliable experimental values, the quantities in Table 1 should represent the best estimates to this date.

The harmonic vibrational frequencies used to compute the ZPEs are also compiled in Table 1. These are computed at the same level of theory as the bond lengths, CCSD(T)/CBS+CV+SO+SR; however, when computing the CBS limit for the bending frequencies, aVDZ-aVQZ basis sets were used, while all other quantities in this table utilized aVTZ-aV5Z sets. It should be noted that CBS frequencies obtained with the two ranges of basis sets were in very close agreement for the bond stretching normal modes. In most cases the difference was less than 1 cm^{-1}, and only in the case of HgI was it larger than 2 cm^{-1}, and it was then only 2.5 cm^{-1}. As was the case for bond lengths, the calculated and experimental harmonic frequencies for the diatomic molecules are in excellent agreement. As opposed to the bond lengths, there do exist accurate harmonic vibrational frequencies for HgCl, HgBr, and HgI. The only molecule in this study for which there is not an accurate

TABLE 2: Relativistic Effects on Dissociation Energies (kcal/mol)[a,b]

molecule	$\Delta E_{\mathrm{SO-TOTAL}}$	$\Delta E_{\mathrm{SO-ZERO}}$	$\Delta E_{\mathrm{SO-diff}}$	ΔE_{Lamb}	ΔE_{SR}	$\Delta E_{\mathrm{DK2-PP}}$	$\Delta E_{\mathrm{DK3-DK2}}$	$\Delta E_{\mathrm{DK3-PP}}$	ΔE_{REL}
HgI	−5.07	−6.82	1.75	0.34		0.20	−0.17	0.03	−4.73
HgBr	−2.26	−3.28	1.02	0.38		0.33	−0.25	0.08	−1.88
HgCl	0.00	−0.86	0.86	0.41	−0.21	0.44	−0.30	0.14	0.20
HgO	1.65	−0.20	1.45	0.35	−0.11	0.23	−0.29	−0.06	1.89
I_2	−12.01	−13.64	1.63	0.09		−0.21	−0.01	−0.22	−11.92
IBr	−8.93	−10.10	1.17	0.06		−0.11	0.00	−0.11	−8.87
ICl	−6.46	−7.68	1.22	0.04	−0.14	−0.10	0.00	−0.10	−6.56
IO	−3.72	−6.45	2.73	0.06	−0.10	−0.42	−0.01	−0.43	−3.76
HgI_2	1.34	0.00	1.34	0.63		−0.63	0.37	−0.25	1.97
HgIBr	1.32	0.00	1.32	0.64		−0.65	0.39	−0.25	1.96
HgICl	0.99	0.00	0.99	0.65	−0.10	−0.70	0.40	−0.28	1.54
HgIO	−0.37	0.21	0.16	0.57	−0.05	−0.94	0.35	−0.59	0.15

[a] $\Delta E_{\mathrm{SO-TOTAL}}$ = total spin−orbit correction; $\Delta E_{\mathrm{SO-ZERO}}$= spin−orbit correction due to the zero-field splitting of the atoms, IO and HgIO; $\Delta E_{\mathrm{SO-diff}}$ = remaining spin−orbit effects calculated from $\Delta E_{\mathrm{SO-TOTAL}} - \Delta E_{\mathrm{SO-ZERO}}$; ΔE_{Lamb} = Lamb-shift correction; ΔE_{SR} = mass velocity + Darwin correction for Cl and O atoms; $\Delta E_{\mathrm{DK2-PP}}$ = difference between reaction enthalpies calculated with pseudopotentials and the second-order DKH Hamiltonian; $\Delta E_{\mathrm{DK3-DK2}}$ = difference between enthalpies calculated with second and third or DKH Hamiltonians; $\Delta E_{\mathrm{DK3-PP}} = \Delta E_{\mathrm{DK2-PP}} + \Delta E_{\mathrm{DK3-DK2}}$; $\Delta E_{\mathrm{REL}} = \Delta E_{\mathrm{SO-TOTAL}} + \Delta E_{\mathrm{Lamb}} + \Delta E_{\mathrm{SR}}$. [b] For the triatomic molecules the reaction HgIX → Hg + IX was used.

experimental harmonic frequency is HgO. The flatness of the potential and the multiple minima on its ground state $\Omega = 0^+$ potential made the calculation of a harmonic frequency for HgO unreliable. Instead, the value listed in Table 1 for HgO is the fundamental vibrational frequency computed numerically with the program LEVEL. The ZPE for this molecule is 217.3 cm^{-1} and was also determined with LEVEL. For the diatomic harmonic frequencies, the RMS of the deviation of theory from experiment is 4.8 cm^{-1} with the largest differences occurring for ICl (7.5 cm^{-1}) and HgI (6.3 cm^{-1}).

Unlike the bond lengths, the vibrational frequencies of the triatomic HgIX molecules have been fairly well characterized experimentally, however, at low resolution. For each mode that has been observed, there is a spread of a few wavenumbers in the experimental values. For the triatomic molecules the calculated harmonic frequencies are compared to experimental fundamental frequencies in Table 1. The comparison, however, should be reasonable due to the small calculated anharmonicity constants of the molecules in this study. Of the molecules that have been observed experimentally, HgICl has the largest calculated anharmonicity constants yet the largest value is only $x_{33} = 1.09$ cm^{-1}. The calculated stretching frequencies are in general slightly higher than the experimental values. The largest difference occurs for the Hg−Cl stretch in HgICl in which the calculated ω_e is 10.4 cm^{-1} higher than the largest experimental value. There is no such general trend for the bending frequencies, but they show similarly good agreement between theory and experiment. The only triatomic for which there is an absence of experimental data is HgIO. A more detailed discussion of the structure and anharmonic spectra of HgX and HgIX (X = O, Cl, Br, I) will be the focus of a future publication.

The relativistic effects on the dissociation energies of each of the molecules included in this study are presented in Table 2. In the case of the triatomic molecules the relativistic contributions correspond to the reaction HgIX → Hg + IX. The final column of this table (ΔE_{REL}) represents the total of the extra relativistic corrections that were applied to the enthalpies of reaction and is equal to $\Delta E_{\mathrm{SO-Total}} + \Delta E_{\mathrm{Lamb}} + \Delta E_{\mathrm{SR}}$, which are described below. Three columns of this table are devoted to the spin−orbit correction. In the first column the total calculated spin−orbit correction ($\Delta E_{\mathrm{SO-Total}}$) is given for each of the reactions. The second column is the contribution of the zero-field splitting of the atoms, as well as those of the $^2\Pi$ IO and HgIO molecules and is denoted $\Delta E_{\mathrm{SO-Zero}}$. The zero-field splitting for the atoms was calculated by taking the difference between the calculated j-averaged levels and the $^2P_{3/2}$ levels for the halogens and the $^3P_2$ level for oxygen. The zero-field splittings of IO and HgIO were calculated as half of the splitting of the calculated $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels. The third column ($\Delta E_{\mathrm{SO-diff}}$) contains the part of the spin−orbit correction not due to this zero-field splitting ($\Delta E_{\mathrm{SO-diff}} = \Delta E_{\mathrm{SO-Total}} - \Delta E_{\mathrm{SO-Zero}}$) and is largely the result of second-order spin−orbit effects. For almost all of the reactions spin−orbit effects are quite large, the two exceptions are in the D_e of HgCl and the reaction HgIO → Hg + IO. The zero spin−orbit correction for HgCl is due to nearly exact cancellation of the zero-field splitting of the Cl atom and the second-order spin−orbit lowering of the molecule. The spin−orbit correction in HgIO is small due to the cancellation of the large calculated zero-field splittings of IO (0.57 kcal/mol) and HgIO (0.78 kcal/mol). When the spin−orbit correction is very large, as in the D_e of I2, most of this correction comes from the zero-field splittings. However, for all of the reactions, except HgIO → Hg + IO, the second-order spin−orbit effects are on the order of 1 kcal/mol or more. Even for the reactions HgI_2 → Hg + I_2, HgIBr → Hg + IBr, and HgICl → Hg + ICl, which involve only closed shell molecules, the spin−orbit correction is 1 kcal/mol or larger. Clearly, it is important to explicitly compute a spin−orbit correction even for closed shell molecules when heavy atoms are involved if accurate results are desired (see also refs 105 and 106).

The fourth column of Table 2 contains the Lamb-shift correction to the dissociation energies. In the four mercury-containing diatomic molecules, mercury goes from an approximately +1 oxidation state in the molecule to a zero-oxidation state in the separated atoms. The Lamb-shift correction to D_e in each of these molecules is nearly the same, ranging from 0.34 kcal/mol in HgI to 0.41 kcal/mol in HgCl. Similarly, in the four triatomic molecule reactions, mercury changes from an approximately +2 oxidation state in the HgIX reactants to a zero oxidation state in the products. The Lamb shifts for all of these reactions are also very similar and approximately two times larger than the correction in the HgX diatomics. These results are similar in magnitude to the correction calculated for the first ionization potential of Hg, −0.78 kcal/mol. It is also interesting to note that the Lamb-shift correction slightly increases with increasing electronegativity of the X-atom as one moves from I to Br to Cl in both the diatomic and triatomic molecules. These observations seem to support the notion that the Lamb shift will be significant in reactions involving changes in s-orbital occupations[94] (i.e., the 6s orbital of mercury in these reactions). In the four dissociation energies that do not involve mercury

TABLE 3: Dissociation Energies for the Diatomic Molecules of This Study (kcal/mol)[a]

molecule	D_e(QZ)	ΔE_e(CBS-QZ)	ΔE_{ZPE}	ΔE_{CV}	ΔE_{CV-f}	ΔE_{REL}	ΔE_{CCSDTQ}	D_0(theory)	D_0(exp)
HgI	12.41	0.96	−0.19	0.26	−0.16	−4.73	[j]	8.55	7.83 ± 0.11[b]
HgBr	17.60	1.00	−0.28	−0.20	−0.19	−1.88	0.25	16.30	15.53 ± 0.29[c]
HgCl	22.77	1.12	−0.43	−0.55	−0.20	0.20	[j]	22.91	23.44[d]
HgO	1.77	1.13	−0.62	0.19	−0.04	1.89	[j]	4.32	
I_2	45.34	2.18	−0.31	0.75		−11.92	[j]	36.04	35.57[e]
IBr	48.90	2.05	−0.39	0.47		−8.87	0.01	42.17	41.93[f]
ICl	54.49	2.04	−0.56	0.10		−6.56	[j]	49.51	49.65[g]
IO	56.22	1.49	−0.98	0.16		−3.76	1.18	54.31	53[h], 56.4[i]

[a] D_e(QZ) = equilibrium dissociation energy calculated with the aVQZ basis set; ΔE_e(CBS-QZ) = difference between aVQZ and CBS CCSD(T) equilibrum dissociation energies; ΔE_{ZPE} = zero-point energy contribution; ΔE_{CV} = core-valence contribution from Hg 5s5p, Br 3s3p3d, and I 4s4p4d; ΔE_{CV-f} = core-valence contribution from Hg 4f; ΔE_{REL} = total relativistic corrections from Table 2; ΔE_{CCSDTQ} = correction for full iterative triple and quadruple excitations. See text. [b] Ref 36. [c] Ref 118. [d] Ref 35, this is a rough upper bound. [e] D_0 = 12440.083 ± 0.145 cm^{-1} from ref 125. [f] D_0 = 14663.8 ± 0.19 cm^{-1} from ref 126. [g] D_0 = 17365.804 ± 0.150 cm^{-1} from ref 127. [h] Ref 107. [i] Ref 110. [j] Not determined.

(I_2, IBr, ICl, and IO), the Lamb-shift correction is never larger than 0.1 kcal/mol, which seems to indicate that it is not very significant even for atoms as heavy as iodine. We have observed similarly small Lamb-shift corrections in preliminary calculations on $CdBr_2$ and CdBr.

The mass velocity + Darwin corrections for the Cl and O atoms are presented in the fifth column of Table 2 under the heading ΔE_{SR}. This correction is in general quite small, with the largest value being −0.21 kcal/mol for the dissociation energy of HgCl. The corrections for the other molecules are generally on the order of 0.1 kcal/mol.

Finally, the three columns in Table 2 labeled ΔE_{DK2-PP}, $\Delta E_{DK3-DK2}$, and ΔE_{DK3-PP} compare enthalpies calculated with pseudopotentials to all-electron calculations. The total energies one obtains with the DK2 and DK3 Hamiltonians can be quite different from each another, especially for molecules as heavy as I_2. For I_2 the MP2 energies with the truncated V5Z-DK basis set are −14222.050801 and −14226.379243 E_h using the DK2 and DK3 Hamiltonians, respectively. However, when energy differences are considered, there is much less difference between DK2 and DK3. In fact, for the molecules not containing mercury, the difference between DK2 and DK3 for the reactions in Table 2 is never larger than 0.01 kcal/mol. In I_2, IBr, and ICl the difference between the DK2 enthalpies and the PP enthalpies are only one or two tenths of a kcal/mol. In IO the difference is much larger at −0.43 kcal/mol. The differences between the DK2 and PP enthalpies for the reactions involving mercury tend to be somewhat larger in magnitude than in the reactions not involving mercury. However, in every case the DK3−DK2 differences are between 0.2 and 0.4 kcal/mol and opposite in sign to the DK2−PP differences. This would seem to suggest that much of the differences between the DK2 and PP calculations are due to inadequacy of the treatment of scalar relativistic effects in the DK2 Hamiltonian when atoms as heavy as mercury are involved. The column ΔE_{DK3-PP} is an estimated difference between DK3 and PP enthalpies obtained by adding the two previous columns. The agreement between DK3 and PP enthalpies appears to be much better than in the DK2 case and is only larger than 0.30 kcal/mol in the HgIO reaction. However we should reiterate that DK2 seems to do well even for atoms as heavy as iodine. As with the Lamb shift, we have observed similarly good agreement between DK2 and DK3 calculations in reactions involving $CdBr_2$ and CdBr.

There are several factors that may contribute to the remaining discrepancy between the all electron and pseudopotential enthalpies. The Dirac-Hartree−Fock calculations against which the pseudopotentials were parametrized include the Breit interaction, finite nucleus effects, and two-electron scalar relativistic effects; these effects are not included in the DKH Hamiltonians used in this study. Also, even though large basis sets of similar quality were employed there are likely small basis set effects involved. Of course, there are also likely small errors due to the frozen core in the pseudopotential calculations as well as the use of nodeless outer-core pseudo-orbitals. Accurately quantifying the errors due to the pseudopotential approximation for heavy elements is thus quite challenging and attempts to make such a correction have not been attempted in this work.

Table 3 contains the calculated and experimental dissociation energies (D_0) of the diatomic molecules involved in this study. Together with the final dissociation energies, each of the individual corrections to the CCSD(T)/CBS energy differences are tabulated. As the results in Table 2 clearly demonstrate, it is insufficient to use only basis sets of even quadruple-ζ quality to obtain highly accurate results. The differences between the D_e values calculated with the aVQZ basis and those at the CBS limit range from 1 to 2 kcal/mol. It should be noted that CBS limit D_e values calculated with the two extrapolation formulas (that were then averaged) typically differ by just 0.2−0.3 kcal/mol with the largest difference (0.5 kcal/mol) occurring in the case of I_2. The inclusion of core-valence correlation also makes significant contributions. The largest total core-valence correlation correction is calculated for the I_2 and HgCl molecules where it is 0.75 kcal/mol in each case. The correlation of the Hg 4f electrons appears to be quite important and is approximately of the same order of magnitude as the correlation of the Hg 5s5p and halogen (n-1)s(n-1)p(n-1)d electrons. The additional relativistic corrections (ΔE_{REL}) have been discussed above.

A wide range of dissociation energies and heats of formation have been reported for the IO molecule. Two independent crossed molecular beam studies of the reaction O + ICl have reported a ΔH_f(0 K) for IO of 32 ± 3 kcal/mol[107] and 30 ± 2 kcal/mol[108] (D_0 = 53 and 55 kcal/mol, respectively). These are slightly higher than those obtained from kinetics studies;[109,110] the reaction between oxygen atom and alkyl iodides places an upper bound on the ΔH_f(298 K) of IO at 28.8 kcal/mol[109] (D_0 = 55.3), while kinetic investigations of the reaction IO + ClO yielded a ΔH_f(298 K) for IO of 27.7 ± 1.2 kcal/mol[110] (D_0 = 56.4 kcal/mol). Previous high quality ab initio investigations have predicted varying 0 K heats of formation of IO, these being 31.0 ± 1.0 kcal/mol,[111] 28.9 ± 1.8 kcal/mol,[112] and 38.9 kcal/mol[113] (D_0 = 53.6, 55.7, 45.7 kcal/mol, respectively). In this work, without the inclusion of higher order electron correlation effects, the CCSD(T)/CBS+CV+SO+SR+LAMB dissociation energy (D_0) of IO is 53.135 kcal/mol. The correction for iterative triple excitations [CCSDT-CCSD(T)] calculated with the aVTZ basis sets was calculated to add 0.50 kcal/mol. The addition of iterative quadruple excitations [CCSDTQ-CCSDT] calculated with the aVDZ basis set was found to yield an additional 0.68 kcal/mol, resulting in a total correction of 1.18 kcal/mol.

TABLE 4: 0 K Enthalpies of Reaction, ΔH_r (kcal/mol), with Constituent Energy Contributions[a]

reaction		ΔE_e(QZ)	ΔE_e(CBS-QZ)	ΔE_{ZPE}	ΔE_{CV}	ΔECV-*f*	ΔE_{REL}	ΔE_{CCSDTQ}	ΔHr	expt[b]
Hg + I_2	→ HgI + I	32.92	1.22	−0.12	0.48	0.16	−7.19	*e*	27.47	27.74 ± 0.11
	→ HgI_2	−32.37	−0.25	0.42	−0.88	0.07	−1.97	*e*	−34.98	−33.4 ± 0.5[c]
Hg + IBr	→ HgI + Br	36.49	1.08	−0.20	0.21	0.16	−4.14	0.01	33.61	34.10 ± 0.11
	→ HgBr + I	31.30	1.04	−0.11	0.67	0.19	−6.99	−0.24	25.86	26.40 ± 0.29
	→ HgIBr	−36.05	−0.43	0.46	−0.64	0.07	−1.96	0.01	−38.54	
Hg + ICl	→ HgI + Cl	42.08	1.08	−0.36	−0.16	0.16	−1.83	*e*	40.97	41.82 ± 0.11
	→ HgCl + I	31.73	0.92	−0.13	0.65	0.20	−6.76	*e*	26.61	26.21
	→ HgICl	−37.54	−0.57	0.52	−0.64	0.07	−1.54	*e*	−39.70	
Hg + IO	→ HgI + O	43.80	0.54	−0.79	−0.10	0.16	0.97	1.18	45.76	45 ± 3[d]
	→ HgO + I	54.45	0.37	−0.36	−0.04	0.04	−5.65	1.18	49.99	
	→ HgIO	−12.28	−0.52	0.50	−0.99	0.02	−0.15	1.18	−12.24	

[a] ΔE_e = CCSD(T) electronic energy difference; ΔE_{ZPE} = zero-point energy contribution; ΔE_{CV} = core-valence contribution from Hg 5s5p, Br 3s3p3d, and I 4s4p4d; ΔE_{CV-f} = core-valence contribution from Hg 4f; ΔE_{REL} = relativistic corrections from Table 2; ΔE_{CCSDTQ} = correction for full iterative triple and quadruple excitations. See text. [b] All experimental data taken from Table 2, except where noted. [c] ΔH_f of HgI_2 from ref 114. [d] ΔH_f of IO derived from ref 107. [e] Not determined.

Combining these values results in our best predicted value for D_0 of 54.31 kcal/mol. Due to the probable underestimation of spin−orbit effects in the atoms as well as errors due to the PP approximation, this value may be slightly too large. To determine the heat of formation, accurate experimental values for the ΔH_f(0 K) of I (25.61 ± 0.01 kcal/mol)[114] and O (58.98 ± 0.02 kcal/mol)[114] were combined with our predicted D_0 of IO to yield a predicted ΔH_f(0 K) for IO of 30.28 kcal/mol. Using standard ideal gas forms of the partition functions, our calculated heat of formation at 298K is 29.81 kcal/mol. This result is in good agreement with the ΔH_f values determined in the molecular beam experiments and two of the previous ab initio calculations, but it is considerably higher than those determined from the kinetics experiments. Based on the accuracy of the other dissociation energies in this study, and similar previous work (see, for instance, refs 14, 105, 115, and 116 and ref 24 cited in Dixon et al.[117]), we believe our calculated ΔH_f(0 K) of IO has an accuracy better than 1 kcal/mol and is the most reliable value to date.

To gauge the effects of higher levels of electron correlation on the other reactions of this study, CCSDT and CCSDTQ corrections have also be calculated for the dissociation energies of IBr and HgBr. In both of these molecules the corrections are significantly smaller than they were in IO. For IBr the CCSDT-CCSD(T) difference is −0.22 kcal/mol, and the CCSDTQ-CCSDT difference is +0.23 kcal/mol. The two corrections essentially cancel each other for a total correction of just 0.01 kcal/mol. In HgBr the total correction is somewhat higher at 0.25 kcal/mol, with 0.21 kcal/mol arising from the CCSDT-CCSD(T) difference and 0.04 kcal/mol from the CCSDTQ-CCSDT difference. These smaller corrections for IBr and HgBr are more representative of the usual quality of CCSD(T) wave functions for molecules dominated by the Hartree−Fock configuration. It is likely that the large correction for higher order correlation effects is isolated to the IO molecule in this study.

Accurate and reliable experimental dissociation energies are available for I_2, IBr, and ICl, and in all three of these cases the agreement between theory and experiment is very good. The largest difference occurs in I_2, where it is only 0.47 kcal/mol. The disagreement between theory and experiment for HgBr, HgCl, and HgI is slightly higher, but in all three cases still much less than 1 kcal/mol. The experimental dissociation energy for HgI (7.83 kcal/mol)[36] has an uncertainty of 0.11 kcal/mol, while the experimental dissociation energy of HgBr (15.53 kcal/mol)[118] has a stated uncertainty of 0.29 kcal/mol. The calculated values of 8.55 kcal/mol for HgI and 16.30 kcal/mol for HgBr fall slightly outside these error bounds. In HgCl the experimental dissociation energy of 23.44 kcal/mol[35] is only a rough upper bound, and the calculated value of 22.91 kcal/mol falls below this value. There has not been a reliable experimental determination of the dissociation energy of the HgO molecule to date. The remaining differences in the experimental and calculated dissociation energies of the molecules in this study can likely be attributed to remaining inadequacies in the treatment of spin−orbit coupling, correlation treatment, pseudopotential approximation, and experimental uncertainties in HgI, HgBr, HgCl, and IO.

The calculated enthalpies of reaction (0 K) along with the various corrections to the CCSD(T)/CBS limits are presented in Table 4 for the reactions Hg + IX (X = I, Br, Cl, O). Each of the corrections to the valence-only CCSD(T) enthalpies are in general small, but have nonnegligible cumulative effects. The difference between energies of reaction computed with the aVQZ basis set (the second largest basis set used), and those at the CBS limit are as large as 1.2 kcal/mol and are never smaller than 0.2 kcal/mol. As with the dissociation energies, reaction enthalpies calculated with the two CBS extrapolation formulas typically differ by just 0.1−0.2 kcal/mol with the largest difference of 0.3 kcal/mol in the reaction Hg + I_2 → HgI +I. The ZPE corrections are in general small, but are as large as 0.8 kcal/mol for the reaction Hg + IO → HgI + O. The mean value of the total CV correction to the enthalpies of reaction is 0.52 kcal/mol and is as large as 0.97 kcal/mol for the reaction Hg + IO → HgIO. The correlation of the Hg 4f electrons is again shown to be important, often as large as 0.2 kcal/mol but is in general smaller than the effect of correlating the outer-core electrons in these reactions. The effect of the CCSDT and CCSDTQ corrections to the bond strengths of IBr, HgBr, and IO were included in the reaction enthalpies of Table 4 where appropriate.

The reaction enthalpies are qualitatively similar to the results of a previous study[14] on the reactions Hg + {Br_2, BrCl, Cl_2, BrO, ClO}. All of the abstraction reactions (i.e., Hg + XY → HgX + Y) are endothermic by 25−45 kcal/mol. Conversely, all of the insertion reactions (i.e., Hg + XY → XHgY) are exothermic by −35 to −40 kcal/mol. However, preliminary MRCI calculations indicate that the direct insertion reactions have large barriers on the order of 25 kcal/mol and are therefore not likely to occur in the atmosphere. However, all of the recombination reactions such as HgX + Y→ XHgY are strongly exothermic by −60 to −80 kcal/mol and are predicted to proceed without a barrier.

Agreement between calculated and experimental enthalpies of reaction is quite good where the experimental values are available. There is only one instance where the calculated enthalpies disagree with experiment by more than 1 kcal/mol;

TABLE 5: Dissociation Energies and 0 K Heats of Formation (in kcal/mol) for HgIX Species[a]

IHgY	D_0(IHg + Y)	D_0(I + HgY)	ΔH_f (calc)	ΔH_f (exp)
IHgI		62.47	−3.91	−2.35 ± 0.50[b]
IHgBr	72.15	64.40	−11.21	
IHgCl	80.67	66.31	−19.71	
IHgO	58.00	62.23	33.46	

[a] Computed from the reaction enthalpies in Table 4 and accurate experimental heats of formation. [b] Ref 114.

the difference between theory and experiment is 1.6 kcal/mol for the reaction $Hg + I_2 \rightarrow HgI_2$, with the calculated result (−34.98 kcal/mol) being more exothermic than the experimental value[114] (−33.4 ± 0.5 kcal/mol). It is possible, however, that the error bounds of the experimental value, which was determined from the heat of formation of the crystal and its heat of sublimation, are overly optimistic. A second reaction with a fairly large discrepancy between theory and experiment, although the difference is less than 1 kcal/mol, is $Hg + ICl \rightarrow HgI + Cl$. In this case the calculated value (40.97 kcal/mol) is more exothermic than experiment (41.81 ± 0.11 kcal/mol) by 0.85 kcal/mol. Due either to large uncertainties or a complete lack of experimental heat of formation data for HgIBr, HgICl, HgIO, HgO, HgCl, and IO, the currently calculated enthalpies for reactions involving these species are the best currently available.

Table 5 contains the calculated dissociation energies and 0 K heats of formation for the triatomic species HgI_2, HgIBr, HgICl, and HgIO. To calculate these heats of formation we used the enthalpies of reaction for $Hg + IX \rightarrow HgIX$ tabulated in Table 3 together with accurate experimental heats of formation for the Hg and IX species. In the case of HgIO, the reaction $Hg + I + O \rightarrow HgIO$ was used instead of $Hg + IO \rightarrow HgIO$ because of the uncertainty in the experimental heat of formation of IO. The atomic and diatomic 0 K heats of formation were taken from JANAF:[114] 15.42 ± 0.01 kcal/mol for Hg, 25.61 ± 0.01 kcal/mol for I, 58.98 ± 0.02 kcal/mol for O, 4.57 ± 0.03 kcal/mol for ICl, 11.91 ± 0.02 kcal/mol for IBr, and 15.65 ± 0.02 kcal/mol for I_2. The only triatomic species for which there exists an experimental heat of formation is HgI_2, and the difference between the experimental and theoretical results (1.6 kcal/mol) is of course the same as that for the reaction $Hg + I_2 \rightarrow HgI_2$.

Conclusions

Accurate ab initio calculations have been performed to determine the thermochemistry of reactions between mercury- and iodine-containing reactive halogen species. These calculations have been performed using high levels of electron correlation and series of correlation consistent basis sets with accurate relativistic pseudopotentials, which allowed for extrapolations to the complete basis set limit. Corrections were also included to account for core-valence correlation, spin−orbit coupling, scalar relativity, the Lamb shift, and in some cases higher levels of electron correlation. We have calculated 0 K heats of formation for the species HgIX (X = I, Br, Cl, O) and heats of reaction for

$$Hg + IX \rightarrow \begin{cases} HgX + I \\ HgI + X \\ IHgX \end{cases}$$

where X = I, Br, Cl, and O. The accuracy of the reported enthalpies is expected to be within 1 kcal/mol, which is for most of the reactions an improvement over existing experimental values. To the best of our knowledge these calculations are the first to characterize gas-phase HgIO.

The heats of reaction for the present iodine-containing reactions are similar in sign and magnitude to the corresponding reactions involving only bromine and chlorine. All of the insertion reactions are found to be strongly exothermic, while the abstraction reactions are all strongly endothermic. If iodine exists in sufficient concentration in the polar tropospheres, it is possible that many of these species and reactions play a role in the episodic mercury depletion events that have recently been observed. The strongly bound IHgX (X = I, Br, Cl, O) species are possible contributors to reactive gaseous mercury concentrations. The formation of IHgX by direct reaction of Hg with IX is unlikely due to the large barriers indicated by preliminary MRCI+Q/aVTZ calculations. Large barriers have also been observed for the insertion of Hg into Br_2 in recent work on the global potential energy surface for HgBr + Br.[119]

The present calculations predict the reactions of HgI + X or HgX + I to form HgIX to be strongly exothermic. Our preliminary MRCI+Q/aVTZ calculations and HgBr + Br PES results suggest these reactions will be barrierless. Other reactions involving initially formed HgX molecules can also lead to the formation of HgXY. For example the current results would predict the following reaction enthalpies

$$HgI + IBr \rightarrow \begin{cases} HgI_2 + Br & \Delta H_r = -20.28 \text{ kcal/mol} \\ HgIBr + I & \Delta H_r = -29.98 \text{ kcal/mol} \end{cases}$$

and

$$HgI + IO \rightarrow \begin{cases} HgI_2 + O & \Delta H_r = -8.14 \text{ kcal/mol} \\ HgIO + I & \Delta H_r = -3.64 \text{ kcal/mol} \end{cases}$$

Preliminary MRCI+Q/aVTZ calculations indicate that each of these reactions should also proceed without a barrier. The current results and the results of our previous work on the reactions Hg + {Br_2, Cl_2, BrCl, BrO, ClO}[14] can be used to calculate the enthalpies of similar reactions involving any combination of I, Cl, and Br. It is hoped these accurate results can be used to advance future atmospheric modeling studies.

As part of this work, accurate dissociation energies have also been calculated for all the diatomic molecules involved in this study. In particular, an accurate heat of formation of IO has been calculated. Our results predict a ΔH_f(298 K) of 29.8 ± 1.0 kcal/mol (D_0 = 54.3 ± 1.0 kcal/mol), which is slightly higher than the value reported in recent kinetics studies, but is in good agreement with earlier crossed molecular beam studies. This purely ab initio result is also in good agreement with the earlier predictions of both McGrath and Rowland[111] and Hassanzadeh and Irikura.[112]

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