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Chemically Accurate Thermochemistry of Cadmium: An ab Initio Study of Cd + XY (X = H, O, Cl, Br; Y = Cl, Br)

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Using a composite coupled cluster method employing sequences of correlation consistent basis sets for complete basis set (CBS) extrapolations and with explicit treatment of core−valence correlation and scalar and spin−orbit relativistic effects, the 0 K enthalpies of a wide range of cadmium−halide reactions, namely, Cd + (HCl, HBr, ClO, BrO, Cl_2, BrCl, Br_2) have been determined to an estimated accuracy of ±1 kcal/mol. In addition, accurate equilibrium geometries, harmonic frequencies, and dissociation energies have been calculated at the same level of theory for all the diatomic (e.g., CdH, CdO, CdCl, CdBr) and triatomic (CdHCl, CdHBr, CdClO, CdBrO, $CdCl_2$, CdBrCl, $CdBr_2$) species involved in these reactions, some for the very first time. Like their mercury analogues, all of the abstraction reactions are predicted to be endothermic, while the insertion reactions are strongly exothermic with the formation of stable linear, Cd-centric complexes. With the exception of CdH and the reactions involving this species, the present results for the remaining Cd-containing systems are believed to be the most accurate to date.

I. Introduction

There has recently been a great deal of interest in the reactions between mercury and reactive halogen species (see, for example, refs 1−3 and references therein). These reactions have been of interest due to their likely involvement in recently observed depletions of atmospheric mercury concentrations in the arctic troposphere during polar spring[4−7] and also these reactions' more general involvement in the global cycling of mercury.[8,9] Cadmium is a toxic heavy metal similar to mercury in that it has long atmospheric residence times and also exhibits long-range transport from its original emission sources.[10] The major natural source of Cd in the atmosphere is volcanic emission.[10,11] The major anthropogenic sources of atmospheric cadmium are comparable to or greater than the natural sources, and the most significant of these are waste incineration and nonferrous metals production.[10] Due to the similarity of the chemistry between mercury and cadmium, it is likely that reactions between cadmium and reactive halogen species play an important role in the global cycling of cadmium. Unlike mercury, however, cadmium exists predominately in the particulate phase in the atmosphere.[10,11] A fundamental understanding of cadmium's gas-phase chemistry is valuable in the understanding of the formation of these particles and also to form a basis for future studies into the heterogeneous chemistry of cadmium. Gas-phase reactions between cadmium and small halogen-containing species are also likely to be important in combustion chemistry and thus of relevance to the primary ways in which cadmium is introduced into the atmosphere.

Despite this potential importance of reactions between cadmium and small halide molecules, very little is known about their gas-phase properties and specifically the thermochemistry of cadmium halides. To broaden the current knowledge of such reactions, this work reports an ab initio investigation of the thermochemistry, equilibrium geometries, and vibrational frequencies of species relevant to the reactions Cd + {HCl, HBr, ClO, BrO, Cl_2, Br_2, and BrCl}, which include the following cadmium-containing products: the diatomic molecules CdH, CdO, CdCl, and CdBr and the triatomic species CdHCl, CdHBr, CdClO, CdBrO, $CdCl_2$, $CdBr_2$, and CdBrCl. The reactions of Cd with HCl and HBr should be particularly important in combustion chemistry. The gas-phase properties of CdHCl and CdHBr are also of particular interest, since ZnHCl was recently the first gaseous metal hydrochloride to be observed experimentally[12] and CdHCl has recently been studied in argon matrices.[13] Diatomic cadmium halides have also received some prior attention due to their lasing properties,[14] analogous to their mercury counterparts.

While accurate thermochemical information was not previously available for many of the species and reactions in this study, there have been a few experimental investigations of gas-phase and matrix-isolated cadmium dihalides. Klemperer[15] first reported the gas-phase infrared (IR) spectra of $CdBr_2$ and $CdCl_2$ in 1956. Givan, Loewenschuss, and co-workers[16−19] conducted a number of IR and Raman studies of matrix-isolated $CdBr_2$, $CdCl_2$, and CdBrCl in the 1970s. There have also been a number of electron diffraction studies that allowed for estimates of the bond lengths in $CdCl_2$ [20] and $CdBr_2$.[21] Further, an early mass spectrometric investigation of CdBrCl allowed researchers to calculate a rough value for its heat of formation.[22]

The diatomic cadmium halides CdBr and CdCl have received considerably less experimental attention and have been limited to studies focused on their electronic spectroscopy.[14,23,24] CdO has been observed in matrices via IR, Raman, and UV−vis spectroscopy[25,26] and has also been studied in the gas phase via mass spectrometry.[27] Unlike the other diatomic cadmium molecules in this study, CdH has been very well characterized in the gas phase.[28]

A number of the molecules in this study have been previously studied theoretically using relatively modest levels of electron correlation and basis sets. The first such calculations were carried out by Stromberg et al.[29] who reported small configuration interaction calculations on $CdCl_2$ using effective core potentials and double-ζ basis sets. Since those first calculations,

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a number of studies have been carried out on CdCl, CdBr, $CdCl_2$, and $CdBr_2$ using semiempirical,[30] DFT,[31,32] and MP2[33] methods with triple-ζ or smaller basis sets. CdHCl has been previously studied with B3LYP and triple-ζ quality basis sets.[13]

In this work, we have used a composite thermochemical approach similar to that used in previous investigations in our group, as well as by Feller, Dixon, and co-workers (cf., refs 34−42 and references therein). Closely related procedures include the recently proposed HEAT method,[43] the W*n* methods of Martin and co-workers,[44] and the focal point technique of Schaefer and co-workers.[45] The present procedure, which has been shown to yield enthalpies accurate to within ± 1 kcal/mol or better, generally involves calculations with coupled cluster theory with extrapolations of these total energies to the complete basis set limit. Further corrections such as core−valence correlation and relativistic effects are then added on the basis of the specific nature of the problem under study. In this work, the additional corrections we include are for core−valence correlation, spin−orbit coupling, scalar relativistic effects, and the pseudopotential approximation. The presently reported heats of reaction are expected to be the most accurate to date for nearly all of the reactions studied. Additionally, with the exception of CdH, the calculated equilibrium structures for all of the cadmium-containing molecules, i.e., CdHCl, $CdCl_2$, CdBrCl, $CdBr_2$, CdO, CdCl, and CdBr, should be the most reliable values currently available. To the best of our knowledge, this is the first report, either experimental or theoretical, for the gas-phase molecules CdBrO, CdClO, and CdHBr.

II. Methodology

In preparation for a subsequent study of their spectroscopic properties, near-equilibrium potential energy surfaces consisting of 74 points around the equilibrium geometries were computed for each of the triatomic molecules. Symmetry considerations reduced the number of points that were explicitly calculated for $CdCl_2$ ($D_{\infty h}$) and $CdBr_2$ ($D_{\infty h}$) to 26, and for the other triatomic molecules ($C_{\infty v}$ with Cd as the central atom), the number of points was reduced to 50. The potential surfaces were fit to polynomials in internal displacement coordinates using the program *SURFIT*.[46] Equilibrium geometries, harmonic frequencies, and anharmonicity constants were then determined from the resulting polynomial coefficients. For the diatomic molecules, a series of seven points were computed about r_e, and the resulting curves were also accurately fit to polynomials. The usual Dunham[47] analysis was utilized to determine the spectroscopic constants. In each case, anharmonic zero-point vibrational energies (ZPEs) were determined from the quartic force fields using the calculated harmonic frequencies and anharmonicity constants.[48]

The first series of calculations that were carried out determined the reaction enthalpies and dissociation energies with the coupled cluster singles and doubles method with a perturbative treatment of triple excitations[49−51] [CCSD(T)] at the complete basis set (CBS) limit. The frozen core approximation was applied in these cases. For all open-shell molecules and atoms, the R/UCCSD(T)[51−53] method was used, i.e., restricted open-shell Hartree−Fock (ROHF) calculations were used to determine the reference wave functions, but the spin restriction was relaxed in the coupled cluster calculations. In the open-shell atomic calculations, the orbitals were symmetry-equivalenced between all three components (P_x, P_y, and P_z) of the ground-state terms. All of the coupled cluster calculations were carried out with the *MOLPRO 2002.6* suite of electronic structure programs.[54]

TABLE 1: Basis Set and Pseudopotential Details

element		basis	exclude from PP core	active AOs
H, O	FC	aug-cc-pVnZ		1s (H), 2s2p (O)
	CV	aug-cc-pwCVTZ		1s (H), 1s2s2p (O)
	FC	aug-cc-pVTZ-DK		1s (H), 2s2p (O)
Cl	FC	aug-cc-pV(n+d)Z		3s3p
	CV	aug-cc-pwCVTZ		2s2p3s3p
	FC	aug-cc-pV(T+d)Z-DK		3s3p
Br	FC	aug-cc-pVnZ-PP	$3s^23p^63d^{10}4s^24p^5$	4s4p
	CV	aug-cc-pwCVTZ-PP	$3s^23p^63d^{10}4s^24p^5$	3s3p3d4s4p
	FC	aug-cc-pVTZ-DK		4s4p
Cd	FC	aug-cc-pVnZ-PP	$4s^24p^64d^{10}5s^2$	4d5s
	CV	aug-cc-pwCVTZ-PP	$4s^24p^64d^{10}5s^2$	4s4p4d5s
	FC	aug-cc-pVTZ-DK		4d5s

The basis sets used in this work are from the systematically convergent correlation consistent family of basis sets. Basis sets of double-ζ through quintuple-ζ quality, augmented with an additional diffuse function of each angular momentum type, were used in these first series of calculations. For oxygen and hydrogen, the basis sets corresponded to the aug-cc-pVnZ sets;[55] for chlorine, the aug-cc-pV(n+d)Z sets[56] that contain modified d-shells containing additional tight exponents; for cadmium[39] and bromine,[57] the aug-cc-pVnZ-PP sets with energy consistent small-core relativistic pseudopotentials (PPs) of the Stuttgart/Köln type.[57,58] The relativistic PP for cadmium replaced 28 electrons leaving the $4s^24p^64d^{10}5s^2$ electrons to be treated explicitly, and that for bromine replaced 10 electrons, leaving the $3s^23p^63d^{10}4s^24p^5$ electrons to be treated. A summary of the electrons excluded from the core and the active atomic orbitals associated with the different basis sets employed in this study is provided in Table 1. The group of basis sets just described will be simply denoted aVnZ (n = D, T, Q, 5) throughout the remainder of the paper. For geometries corresponding to linear structures, all four basis sets from aVDZ to aV5Z were used, but for bent triatomic geometries, the largest basis set employed was aVQZ. The systematic convergence of these basis sets was exploited to obtain an estimate of the CBS limit for the total energies using two extrapolation formulas

$$E(n) = E_{\mathrm{CBS}} + B\,\mathrm{e}^{-(n-1)} + C\,\mathrm{e}^{-(n-1)^2} \tag{1}$$

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

In eq 1,[59,60] the three largest basis sets used at that geometry were used in the extrapolation, while for the second formula,[61,62] two basis sets were used. Total energies were used in each case. The best estimate of the CBS limit was taken as the average of the two extrapolation procedures, and the spread in these two limits provided an approximate uncertainty in the basis set extrapolation, since eq 1 generally underestimates the true limit, while, on average, eq 2 overestimates.[42]

After obtaining CCSD(T) potential surfaces at the CBS limit, the first correction taken into account was for core−valence correlation, ΔCV. When including correlation of the core electrons, triple-ζ basis sets of the weighted core−valence type were used. For oxygen and chlorine, the aug-cc-pwCVTZ[63] sets were utilized, while the aug-cc-pwCVTZ-PP basis sets were employed for cadmium[39] and bromine.[64] Henceforth, these sets will be denoted awCVTZ. At each geometry, two CCSD(T) calculations were carried out with these awCVTZ basis sets, one in which only the valence electrons were correlated and a second with all electrons correlated except the 1s electrons of chlorine. A core−valence correction was then calculated for each point on the potential surface by taking the difference of these two resulting energies. The ΔCV corrections were only determined for linear geometries.

TABLE 2: Calculated CCSD(T) Equilibrium Bond Lengths (Å)[a]

species			aV5Z	ΔCBS[b]	ΔCV	ΔSO	ΔDK	theory	expt.
$X^1\Sigma^+_{0+}$	HCl		1.2759	−0.0003	−0.0014	0.0000	−0.0001	1.2741	1.2746[95 c,85,96]
$X^1\Sigma^+_{0+}$	HBr		1.4190	−0.0000	−0.0049	0.0004	−0.0005	1.4140	1.4145[85,97]
$X^1\Sigma^+_{g0+}$	Cl_2		1.9926	−0.0033	−0.0035	0.0001	0.0015	1.9873	1.9880[85,98]
$X^1\Sigma^+_{g0+}$	Br_2		2.2922	−0.0034	−0.0097	0.0021	0.0008	2.2819	2.2810[85,99]
$X^1\Sigma^+_{0+}$	BrCl		2.1431	−0.0036	−0.0061	0.0013	0.0007	2.1354	2.1361[85,100]
$X^2\Pi_{3/2}$	ClO		1.5702	−0.0029	−0.0028	−0.0006	0.0018	1.5657[d]	1.5689[101]
$X^2\Pi_{3/2}$	BrO		1.7220	−0.0024	−0.0034	−0.0024	0.0002	1.7140[d]	1.7172[85,102]
$X^2\Sigma^+_{1/2}$	CdH		1.7602	−0.0002	−0.0064[d]	−0.0014	−0.0002	1.7519[e]	1.7611[28,c]
$X^1\Sigma^+_{0+}$	CdO		1.9112	−0.0020	−0.0070	−0.0006	0.0013	1.9030	
$X^2\Sigma^+_{1/2}$	CdCl		2.3397	−0.0023	−0.0050	−0.0004	−0.0004	2.3329	
$X^2\Sigma^+_{1/2}$	CdBr		2.4752	−0.0022	−0.0094	−0.0002	0.0010	2.4664	
$X^1\Sigma^+_{g0+}$	$CdCl_2$		2.2572	−0.0019	−0.0063	−0.0005	0.0002	2.2487	2.21[81], 2.266[82], 2.282[20]
$X^1\Sigma^+_{g0+}$	$CdBr_2$		2.3886	−0.0017	−0.0103	−0.0003	0.0006	2.3768	2.372[80], 2.394[21]
$X^1\Sigma^+_{0+}$	CdBrCl	r_e(CdBr)	2.3834	−0.0018	−0.0103	−0.0003	0.0006	2.3716	
		r_e (CdCl)	2.2622	−0.0019	−0.0063	−0.0005	0.0001	2.2537	
$X^1\Sigma^+_{0+}$	HCdCl	r_e (CdCl)	2.2753	−0.0019	−0.0059	−0.0006	−0.0004	2.2665	
		r_e (CdH)	1.6467	−0.0002	−0.0072	−0.0006	0.0000	1.6388	
$X^1\Sigma^+_{0+}$	HCdBr	r_e (CdBr)	2.4034	−0.0017	−0.0101	−0.0005	0.0002	2.3914	
		r_e (CdH)	1.6529	−0.0001	−0.0073	−0.0006	−0.0003	1.6446	
$X^2\Pi_{3/2}$	CdClO	r_e (CdCl)	2.2543	−0.0019	−0.0067	−0.0006	0.0003	2.2455	
		r_e (CdO)	1.9811	−0.0015	−0.0066	−0.0011	0.0010	1.9730	
$X^2\Pi_{3/2}$	CdBrO	r_e (CdBr)	2.3808	−0.0018	−0.0107	−0.0005	0.0006	2.3685	
		r_e (CdO)	1.9855	−0.0015	−0.0064	−0.0012	0.0010	1.9775	

[a] See the text for the definition of the individual contributions. The best predicted value is given by aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK. Expected uncertainty in the theoretical values is ±0.005 Å. [b] Difference between the estimated CBS limit and the aV5Z value. See the text. [c] Calculated from U_{01}. [d] See also ref 79. [e] The best theoretical estimate for ΔCV is −0.0040 Å, which yields an r_e of 1.7543 Å.

The next contribution considered was for spin−orbit coupling, ΔSO, where aVTZ basis sets were used throughout. For Cd and Br, the one-electron spin−orbit operators were taken from the PPs used in the calculations described above. In the cases of O and Cl, PPs were also used in the SO calculations. Both the Cl[65,66] and O[67] PPs were of the large core, Stuttgart/Köln variety, leaving just the valence electrons to be explicitly treated. The Cl and O basis sets used in these cases corresponded to the aVTZ sets described above, but were recontracted in the presence of the PPs. The multireference configuration interaction method with single excitations (MRCIS) was used with standard valence complete active spaces to determine the spin−orbit corrections. This combination of method and basis set was found to give accurate results in our previous work on the thermochemistry of mercury halides.[41] As in that work, the spin−orbit CI code[68] implemented in the *COLUMBUS* suite of ab initio programs[69] was used. The spin−orbit-MRCIS (SO-MRCIS) calculations utilized sets of natural orbitals determined from single reference configuration interaction singles and doubles (CISD) calculations carried out with *MOLPRO*. The spin−orbit correction was calculated as the energy difference between a MRCIS calculation without the SO operator and a SO-MRCIS calculation that mixed all singlet and triplet (or doublet and quartet) configurations. The ΔSO corrections were also only determined for linear geometries.

While small-core relativistic PPs provide a convenient and accurate technique to account for relativistic effects in atoms and molecules, the loss of nodal structure in the orbitals can introduce small errors in such calculations (cf., refs 70, 71). To approximately account for this effect, energy differences calculated with the PP approach using the aVTZ basis sets have been compared to values determined using the all-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[72,73] In these latter calculations, the Cd basis set corresponded to a newly developed aug-cc-pVTZ-DK set[39] where the exponents and contraction coefficients were optimized using the DKH Hamiltonian. Standard aug-cc-pVTZ basis sets[74] recontracted[75] in atomic DKH calculations were employed for the other atoms (H, O, Cl, Br). These combinations of basis sets will henceforth be denoted as aVTZ-DK. The difference in reaction enthalpies calculated at the CCSD(T)/aVTZ and DKH-CCSD(T)/aVTZ-DK levels of theory yielded the final correction ΔDK. It is important to note that the ΔDK term implicitly includes not only a correction for the pseudopotential approximation, but also one for the small scalar relativistic effects arising from the atoms not treated by PPs (H, O, and Cl), which are treated nonrelativistically in the PP calculations.

One possible remaining concern is that the DKH Hamiltonian does not treat scalar relativistic effects to a sufficient level of accuracy for the Cd-containing molecules to reliably compare the all-electron energy differences (and geometries) with the PP results. This was investigated by calculating reaction energies using the second- (DK2) and third-order (DK3) Douglas−Kroll Hamiltonians[76] for the reactions $Cd + Br_2 \rightarrow CdBr_2$, $CdBr + Br \rightarrow CdBr_2$, and $Cd + Br \rightarrow CdBr$. These calculations were performed at the MP2 level of theory using aVTZ-DK basis sets with the *GAMESS*[77] suite of electronic structure programs. In all three of these reactions, the differences between the DK2 and DK3 results were less than 0.01 kcal/mol. These results are consistent with our previous study,[41] where it was found that, while for mercury there were non-negligible differences between DK2 and DK3 dissociation and reaction energies, DK2 was sufficient up through iodine.

III. Results and Discussion

A. Molecular Structures. Table 2 contains the calculated and experimental equilibrium bond lengths for the 11 diatomic and 7 triatomic molecules involved in this study. The best theoretical values were determined at the CCSD(T)/CBS level of theory with contributions due to core−valence correlation (ΔCV), spin−orbit coupling (ΔSO), and a correction for the pseudopotential approximation and scalar relativity on the light atoms (ΔDK). Table 2 shows the best directly calculated value, CCSD(T)/aV5Z, as well as the effect of the CBS extrapolations (ΔCBS), the effects of each of the other three corrections noted above, and the final predicted results (aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK). In every case, the CCSD(T)/aV5Z bond lengths are longer than the best estimates, and in some cases, considerably so. The corrections for basis set incompleteness and core−valence correlation have the largest effects and always result in bond-length shortening. With the exception of H-containing bonds, the CBS extrapolation typically results in a shortening of about −0.002 Å relative to the aV5Z bond lengths, with some molecules (Cl_2, Br_2, and $BrCl_2$) having ΔCBS values as large as −0.004 Å. The typical magnitude of the core−valence correction on the bond lengths was even larger, with an average value of −0.007 Å for the 23 bond lengths listed in Table 2. The largest core−valence corrections were for the Br-containing bonds due to the relatively large effect of correlating the 3d electrons.

In contrast to the two previously discussed corrections to the valence-only CCSD(T)/aV5Z bond lengths, the contributions due to molecular spin−orbit coupling were significantly smaller. In only six cases was the magnitude of this correction larger than 0.001 Å. The largest was for Br_2 (−0.0021 Å) and BrO (−0.0024 Å). It was perhaps a little surprising that the heavier Cd atom did not result in larger spin−orbit effects, but this presumably reflects the lack of 5p character in these systems. The ΔDK corrections (scalar relativity on H, Cl, and O and the pseudopotential approximation) were also very small and never larger than about 0.001 Å.

Accurate experimental values appear to only be available for CdH and the non-Cd containing molecules. In these cases, each of the calculated values agree, in general, very well with experiment. The largest differences occur for ClO ($\Delta r_e = 0.0041$Å), BrO ($\Delta r_e = 0.0034$Å), and CdH ($\Delta r_e = 0.0092$ Å). However, ClO, BrO, and CdH were the only molecules in this study where the T_1 diagnostic[78] was larger than 0.03, and hence, much of these differences with experiment are likely due to higher-order electron correlation effects. In fact, recent CCSDT and CCSDTQ calculations on ClO and BrO by the present authors have shown that more extensive electron correlation completely removes the remaining discrepancy with experiment in these cases.[79] Even with the relatively high CCSD T_1 diagnostic for CdH, the disagreement in the calculated and experimental bond lengths was a little surprising, since, as discussed below, the harmonic frequencies and dissociation energies agree with experiment to within 2 cm^{-1} and 0.1 kcal/mol, respectively. The potential curve of this molecule is rather flat, however, which makes the r_e value very sensitive to relatively small contributions such as higher electron correlation effects. To further investigate some of the sources of this error, all-electron DK calculations were also carried out for ΔCV using aug-cc-pwCVTZ-DK basis sets. This yielded a core−valence correction for r_e of just −0.0040 Å for CdH in comparison to the PP value as shown in Table 2 of -0.0064 Å. This decreases the disagreement with experiment to 0.0066 Å, much of which could now presumably be accounted for by higher electron correlation effects upon comparison to the ClO and BrO results. Larger basis set (aug-cc-pwCVQZ-PP) core−valence calculations were also carried out on CdH, but this yielded negligible differences in ΔCV for r_e (<0.0001 Å) from the aug-cc-pwCVTZ-PP value. It should also be noted that DK calculations for ΔCV were also carried out for CdBr and $CdBr_2$ to determine if this would lead to systematically better agreement with experiment for the other equilibrium bond lengths of this study, but the differences from the PP results in these cases were only 0.001 Å. This was not deemed large enough to warrant the recalculation of ΔCV for the remaining molecules of this study. Additionally, the difference in ΔCV computed with pseudopotentials or DK for ω_e was only 2 cm^{-1} for CdBr and the ΔCV's for the latter molecule's dissociation energy only differed by 0.07 kcal/mol.

TABLE 3: Harmonic Vibrational Frequencies and Zero Point Energies (cm^{-1})

species		ω_e [a] (theory)	ω_e (expt.)	anharmonic ZPE (theory)
HCl		2997.7	2990.9[85,95]	1485.8
HBr		2650.7	2649.6[103]	1314.2
Cl_2		565.2	559.7[85,98]	282.0
Br_2		328.3	325.3[85,99]	163.9
BrCl		449.0	444.3[85,100]	224.1
ClO		865.1[b]	855.5[101]	431.2
BrO		739.5[b]	732.9[102]	368.6
CdH		1462.7	1460.9[28]	718.9
CdO		614.4	645.1[26]	306.2
			654.4[26]	
CdCl		334.7	331.0[85]	167.0
CdBr		233.2	230.0[23]	116.4
			231.0[24,85]	
$CdCl_2$	(Σ_g)	344.3	329.8[17]	477.1
	(Π_u)	87.0	88.0[18]	
	(Σ_u)	439.0	419[16]	
$CdBr_2$	(Σ_g)	213.9	209.1[17]	334.5
	(Π_u)	63.5	62[18]	
	(Σ_u)	329.5	319[16]	
CdBrCl	(CdBr)	255.4	246.6[17]	406.4
	(bend)	75.6	72.0[18]	
	(CdCl)	407.8	392.9[17]	
CdHCl	(CdCl)	381.3	364.5[13]	1559.0
	(bend)	422.1	432.3[13]	
	(CdH)	1920.5	1890.0[13]	
CdHBr	(CdBr)	270.0		1480.9
	(bend)	407.6		
	(CdH)	1903.5		
CdClO	(CdCl)	381.9		598.3
	(bend)	111.2		
	(CdO)	594.9		
CdBrO	(CdBr)	269.8		528.7
	(bend)	101.3		
	(CdO)	584.8		

[a] Calculated at the CCSD(T)/CBS + ΔCV + ΔSO level of theory. See the text. [b] See also ref 79.

All of the triatomic molecules of this study were found to have linear equilibrium geometries with Cd as the central atom, in agreement with previous theoretical and experimental investigations. However, as can be seen in Table 3, these species generally have fairly small bending force constants, and only CdHBr and CdHCl have bending harmonic frequencies larger than about 100 cm^{-1}. Only the molecules $CdCl_2$ and $CdBr_2$ have experimentally reported bond lengths, and for both molecules the values come from X-ray diffraction experiments.[20,21,80−82] The experimental bond lengths for $CdCl_2$ are fairly disparate, having values of 2.21 Å, 2.266 Å, and 2.282 Å. The presently calculated value of 2.249 Å lies within this range, but does not agree particularly well with any of the experimental values. In the case of $CdBr_2$, our predicted value of 2.377 Å also falls within the range of the two sets of experimental bond lengths, 2.372 Å and 2.394 Å. Unlike $CdCl_2$, the calculated $CdBr_2$ value is in good agreement with one of the experimental results. Due to the high level of the current calculations, our predicted bond length of 2.249 Å for $CdCl_2$ is certainly the most reliable to date and has an expected uncertainty of about ±0.005 Å.

In addition to the experimental data, there have been a small number of previous theoretical predictions of bond lengths for the cadmium molecules in this study. Configuration interaction (CI) calculations carried out by Stromberg et al.[29] yielded a bond length of 2.32 Å for $CdCl_2$ in what were sophisticated calculations for the time. In 1995, Liao et al.[31] reported density functional theory (DFT) calculations employing double-ζ quality basis sets to predict bond lengths for CdCl (2.38 Å), CdBr (2.52 Å), $CdCl_2$ (2.28 Å), and $CdBr_2$ (2.41 Å). These values are in qualitative agreement with our current values, but are larger by 0.03 to 0.05 Å. These results seem reasonable in light of the differences in electron correlation and basis set completeness. Also, in the mid-1990s, Kaupp and von Schnering[33] carried out MP2 calculations with double-ζ basis sets and determined bond lengths of 2.369 Å for CdCl and 2.292 Å for $CdCl_2$, in approximate agreement with the previously mentioned DFT calculations. CdO was also studied by DFT methods at approximately the same time by Chertihin and Andrews,[26] and their resulting bond length of 1.924 Å was also slightly longer but in qualitative agreement with our predicted value of 1.903 Å. More recently, Zhao et al.[32] have carried out DFT calculations on $CdCl_2$ and $CdBr_2$, and these were of similar quality to the other earlier work.

In the case of CdH, theoretical bond lengths have been previously reported using multireference second-order configuration interaction[83] (MR-SOCI) (1.761 Å), MP2[33] (1.739 Å), and four-component CCSD[84] (1.778 Å). The MR-SOCI value of Balasubramanian[83] agrees very well with experiment, but this is probably partly due to a fortuitous cancellation of errors, since their calculated harmonic frequencies and dissociation energies were not in as close agreement. Last, the CdHCl molecule was previously studied via DFT using triple-ζ quality basis sets,[13] and those calculations predicted a H−Cd bond length of 1.673 Å and a Cd−Cl bond length of 2.362 Å, which are both considerably longer than the values calculated here (1.639 Å and 2.267 Å, respectively).

In general, the predicted equilibrium structures of the present work are a considerable improvement over the previously calculated results for the Cd-containing molecules of the present study. With the exception of CdH, the predicted bond lengths of this work are expected to be accurate to within about ±0.005 Å.

B. Vibrational Frequencies. The harmonic vibrational frequencies are compiled along with the available experimental values in Table 3. The theoretical anharmonic zero-point energies are also shown. Accurate experimental harmonic frequencies have been reported for all of the diatomic molecules except CdO. In general, the agreement between theory and experiment is excellent. The largest differences are again for ClO and BrO, which only differ from experiment by $+9.6$ cm^{-1} and $+6.6$ cm^{-1}, respectively. The fact that the harmonic frequencies are too large for ClO and BrO is consistent with their theoretical bond lengths being too short. Chertihin and Andrews[26] derived a gas-phase fundamental vibrational frequency for CdO of 650 ± 10 cm^{-1} based on matrix-isolated infrared studies of the products observed from reactions of laser-ablated Cd atoms with O_2. The bands actually observed were at 645.1 cm^{-1} and 654.4 cm^{-1} for what they believed to be CdO in solid argon and solid nitrogen, respectively. Using the theoretical harmonic frequency for CdO in Table 3 and a calculated anharmonicity constant, $\omega_e x_e = 3.9$ cm^{-1}, yields a theoretical fundamental vibrational frequency of 607 cm^{-1}, which is 43 cm^{-1} lower than the experimental estimate. The specific reason for this large disagreement is not entirely clear. It is possible the experimental bands were strongly blue-shifted due to matrix interactions or even other molecules in the matrices.

For the most part, experimental high resolution gas-phase vibrational frequencies also do not exist for the triatomic molecules in this study. The experimental values for $CdCl_2$, $CdBr_2$, and CdBrCl correspond to fundamental vibrational frequencies taken from matrix-isolated infrared and Raman experiments.[16−19] The theoretical gas-phase harmonic frequencies of Table 3 are in good qualitative agreement with these fundamentals. The largest differences are observed for $CdCl_2$ where the symmetric and antisymmetric stretches differ by 15 cm^{-1} and 20 cm^{-1}, respectively. As one might expect, the theoretical values are larger in all cases (except the $CdCl_2$ bending mode) due primarily to red-shifting of the experimental values from matrix interactions and to a lesser extent the neglect of anharmonicities in the theoretical values; the calculated anharmonicities were in all cases small and generally much less than 1 cm^{-1}. CdHCl has also recently been investigated in matrices with IR and UV−vis spectroscopic methods.[13] The experimental values for this molecule in Table 3 correspond to the harmonic vibrational frequencies. Again, the theoretical and experimental values are in good qualitative agreement, with the theoretical gas-phase values being larger than the experimental matrix-isolated frequencies. Neither CdHBr, CdClO, nor CdBrO have been previously studied by theory or experiment.

Previous theoretical work has yielded harmonic vibrational frequencies for many of these cadmium-containing molecules. CdCl and CdBr frequencies have been previously calculated by DFT, yielding values of 305 and 214 cm^{-1}, respectively.[31] These results differ from the experimental values by 30 and 16 cm^{-1}, respectively, while the current CCSD(T) results differ by just 4 and 3 cm^{-1}. A CdO harmonic frequency has also been calculated with DFT,[26] which yielded a value of 598 cm^{-1}, 16 cm^{-1} smaller than the currently predicted value shown in Table 3. Consistent with the DFT bond lengths that were much too long compared to the present results, the DFT harmonic frequencies are generally significantly smaller than the CCSD(T)/CBS+CV+SO results. DFT harmonic frequencies have also been calculated for $CdCl_2$,[31,32] $CdBr_2$,[31,32] CdBrCl,[32] and CdHCl,[13] and these are also significantly smaller than the currently calculated values, as well as the experimental matrix isolation results. The previous MR-SOCI[83] calculations on CdH resulted in a harmonic frequency of 1524 cm^{-1}, while four-component CCSD[84] yielded a value of 1370 cm^{-1}. By comparison, the current CdH harmonic frequency obtained with our composite approach was calculated to be 1462 cm^{-1}, which is nearly identical to the experimental (harmonic) infrared value of 1461 cm^{-1}.

C. Dissociation Energies and Reaction Enthalpies. The dissociation energies, D_0, for the 11 diatomic molecules of this work are shown with their individual contributions in Table 4, where they are also compared to the best available experimental values. The latter were available for the 7 non-cadmium-containing molecules, as well CdH. In all of these cases, the agreement between theory and experiment is excellent. The largest difference between theory and experiment is just $+0.26$ kcal/mol for Br_2. It should be noted that the ClO and BrO dissociation energies include corrections from CCSDTQ calculations taken from ref 79. Huber and Herzberg[85] give uncertain values for the dissociation energies of CdO (an upper bound of 88 kcal/mol vs the calculated value of 21.71 kcal/mol), CdBr

TABLE 4: CCSD(T) Dissociation Energies (D_0) of the Diatomic Molecules of the present work compared to the available experimental values (kcal/mol)[a]

species	aV5Z	ΔCBS[b]	ΔCV	ΔSO	ΔDK	ΔE_{ZPE}	theory	expt.
HCl	107.25	0.35	0.06	−0.86	−0.25	−4.25	102.29	102.24[85,94]
HBr	92.78	0.29	0.44	−3.18	0.07	−3.76	86.63	86.62[94]
Cl_2	58.98	1.02	−0.02	−1.72	−0.18	−0.81	57.26	57.18[85]
Br_2	51.19	0.88	0.32	−6.26	0.05	−0.47	45.71	45.45[85,104]
BrCl	55.33	0.93	0.09	−3.94	−0.11	−0.64	51.66	51.53[91,105,d]
ClO	63.83	0.83	0.06	−0.61	−0.25	−1.22	63.38[c]	63.43[85,92]
BrO	57.31	0.68	−0.05	−2.05	−0.10	−1.05	55.73[c]	55.21,[106] 55.9[93]
CdH	17.81	0.01	−0.21	0.13	−0.10	−2.06	15.58	15.64[85]
CdO	22.30	0.50	−0.58	−0.12	−0.39	−0.88	20.83	
CdCl	45.12	0.56	−0.91	−0.78	−0.38	−0.48	43.14	
CdBr	37.25	0.55	−0.44	−3.04	−0.11	−0.33	33.88	

[a] See the text for the definition of the individual contributions. The best predicted value is given by aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK + ΔE_{ZPE}. [b] Difference between the estimated CBS limit and the aV5Z value. See the text. [c] These contain additional contributions of +0.72 and +0. 99 kcal/mol for ClO and BrO, respectively, for the effects of iterative triple and quadruple excitations, as well as full CI corrections, to the CCSD(T) values. The core-valence corrections in these cases also used core-valence quadruple-ζ basis sets. See ref 79. [d] D_e was converted to D_0 using the experimental anharmonic zero point energy. See Table 3 for the experimental references.

(21−37 kcal/mol vs the calculated value of 34 kcal/mol), and CdCl (∼49 kcal/mol vs the calculated value of 43.6 kcal/mol). To our knowledge, reliable experimental dissociation energies for these molecules do not exist.

As with the bond lengths, the largest corrections to the dissociation energies are from basis set incompleteness and core−valence correlation. The effect of increasing the basis set from quintuple-ζ to the CBS limit is estimated to generally increase the dissociation energies by about 0.5−1 kcal/mol. The exception to this trend is CdH where the difference between the aV5Z D_e and the CBS limit was calculated to be just 0.02 kcal/mol. The basis set convergence is very fast for this molecule; the difference in D_e between aVTZ and aVQZ is only 0.4 kcal/mol, while the average for the other 10 molecules is 2.2 kcal/mol. The core−valence corrections follow no clear trend and range from +0.44 to −0.91 kcal/mol, with the covalent molecules having core−valence effects tending to increase dissociation energies while the more ionic molecules tend to have negative core−valence corrections.

As observed in Table 4, the corrections to the diatomic D_e's for spin−orbit coupling can be rather large, especially for molecules that contain bromine. The majority of this effect, however, is due to the zero-field splitting of the atoms, as well as first-order splittings in the $^2\Pi$ states of ClO and BrO. It is probable that the magnitude of the spin−orbit correction is underestimated in the present calculations. The zero-field splitting of the atoms can give some estimate of the error in the spin−orbit corrections. The differences between the calculated J-averaged level and the $J = {}^3/_2$ level for the Br and Cl atoms are 3.28 and 0.87 kcal/mol. The experimental values for these differences are 3.51 and 0.84 kcal/mol. Thus, the spin−orbit correction is too small for Br atom by 0.23 kcal/mol and would suggest that the magnitude of the negative spin−orbit correction in the dissociation energies is slightly underestimated. This may partly explain the dissociation energies for Br_2 and BrCl being larger than the experimental values by 0.27 and 0.13 kcal/mol.

As with the bond lengths, the effect due to scalar relativity on H, O, and Cl together with the correction for the PP approximation (ΔDK) is relatively small but non-negligible. Scalar relativistic effects on D_e from Cl amount to about −0.2 kcal/mol (see, for example, HCl, ClO, and Cl_2, which do not involve pseudopotentials), while the corrections for the pseudopotential approximation are estimated to be at most a few tenths of a kcal/mol.

Reaction enthalpies at 0 K are given in Table 5 for the gas-phase reactions

$$\mathrm{Cd} + \mathrm{XY} \rightarrow \begin{cases} \mathrm{CdX} + \mathrm{Y} \\ \mathrm{CdY} + \mathrm{X} \\ \mathrm{XCdY} \end{cases}$$

where X = {Cl, Br} and Y = {H, O, Cl, Br}. For most of the reactions, it is not possible to compare with experiment, because reliable experimental heats of formation are not available for most of the cadmium halide molecules. It was possible, however, to derive accurate experimental enthalpies for Cd + HBr → CdH + Br and Cd + HCl → CdH + Cl based on the accurate experimental dissociation energies for CdH, HCl, and HBr. The agreement between theory and experiment for these two reactions is excellent, with differences of just +0.07 and +0.14 kcal/mol, respectively.

Experimental heats of formation at 298 K for $CdBr_2$ and $CdCl_2$ are given in ref 86, who cite ref 87, but no uncertainties are provided nor is it stated by what means the enthalpies are determined. Converting these values to 0 K, however, using standard ideal gas forms of the partition functions and combined with accurate 0 K heats of formation for Cd(g) (28.20 ± 0.05 kcal/mol)[88,89] and Br_2 (10.92 ± 0.03 kcal/mol)[90] yielded experimental 0 K enthalpies for $\mathrm{Cd} + \mathrm{Cl_2} \rightarrow \mathrm{CdCl_2}$ and $\mathrm{Cd} + \mathrm{Br_2} \rightarrow \mathrm{CdBr_2}$ of −73.8 and −70.1 kcal/mol, respectively. These differ from our calculated values (see Table 5) by −3.2 kcal/mol and +1.0 kcal/mol, respectively. On the basis of the agreement between theory and experiment for the diatomic dissociation energies and the Cd + HCl and Cd + HBr reactions, it is expected that the final theoretical reaction enthalpies in Table 5 should be accurate to at least ± 1 kcal/mol. Hence, the cited experimental heat of formation for $CdCl_2$ may have a relatively large uncertainty.

The enthalpies in Table 5 are qualitatively similar to previous work on the reactions between Hg and the same halogen species[34] (not including HCl and HBr). All of the abstraction reactions (Cd + XY → CdX + Y) are endothermic, while the insertion reactions (Cd + XY → XCdY) are exothermic. One major difference between the mercury and cadmium reactions is that the abstraction reactions with cadmium are significantly less endothermic than the mercury cases due to the larger dissociation energies of the cadmium halides compared to the mercury halides. All of the mercury abstraction reactions involving Br_2, Cl_2, and BrCl were calculated to be endothermic

TABLE 5: Calculated 0 K Reaction Enthalpies Compared to the Available Experimental Values (kcal/mol)[a]

reaction		ΔE_e (aV5Z)	ΔCBS[b]	ΔCV	ΔSO	ΔDK	ΔE_{TQ}[c]	ΔE_{ZPE}	ΔH_r	expt.
Cd + Br_2	→ CdBr + Br	13.94	0.33	0.76	−3.22	0.16		−0.14	11.82	
	→ $CdBr_2$	−69.75	−0.29	0.26	−0.03	0.24		0.49	−69.08	−70.08[86]
Cd + Cl_2	→ CdCl + Cl	13.86	0.46	0.89	−0.94	0.20		−0.33	14.14	
	→ $CdCl_2$	−78.66	−0.19	0.85	−0.12	0.55		0.56	−77.00	−73.80[86]
Cd + BrCl	→ CdBr + Cl	18.08	0.38	0.53	−0.90	0.00		−0.31	17.77	
	→ CdCl + Br	10.21	0.37	1.00	−3.16	0.27		−0.16	8.53	
	→ CdBrCl	−73.97	−0.26	0.50	0.00	0.38		0.52	−72.83	
Cd + BrO	→ CdBr + O	20.06	0.13	0.48	0.86	0.02	0.99	−0.72	21.82	
	→ CdO + Br	35.01	0.18	0.62	−2.06	0.30	0.99	−0.18	34.86	
	→ BrCdO	−45.98	−0.27	0.24	1.09	0.24	0.99	0.46	−43.23	
Cd + ClO	→ CdCl + O	18.71	0.28	1.03	0.17	0.15	0.72	−0.76	20.30	
	→ CdO + Cl	41.53	0.34	0.70	−0.49	0.16	0.72	−0.36	42.61	
	→ CdClO	−47.92	−0.13	0.77	0.27	0.38	0.72	0.48	−45.44	
Cd + HBr	→ CdBr + H	55.53	−0.26	0.88	−0.14	0.18		−3.42	52.76	
	→ CdH + Br	74.97	0.28	0.65	−3.31	0.17		−1.70	71.06	70.99[d]
	→ CdHBr	−16.82	−0.35	0.13	−0.17	0.14		0.48	−16.60	
Cd + HCl	→ CdCl + H	62.13	−0.21	0.97	−0.08	0.13		−3.77	59.17	
	→ CdH + Cl	89.44	0.34	0.27	−0.99	−0.15		−2.19	86.72	86.60[d]
	→ CdHCl	−11.45	−0.31	0.20	−0.16	0.10		0.21	−11.42	

[a] See the text for the definition of the individual contributions. The best predicted value is given by aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK + ΔE_{TQ} + ΔE_{ZPE}. [b] Difference between the estimated CBS limit and the aV5Z value. See the text. [c] Contributions from CCSDT, CCSDTQ, and full CI on ClO and BrO. See ref 79. [d] Calculated from the experimental dissociation energies in Table 4.

TABLE 6: Dissociation Energies and 0 K Heats of Formation in kcal/mol for Triatomic Cadmium Halides[a]

XCdY	D_0(XCd+Y)	D_0(X+CdY)	ΔH_f (calcd)	ΔH_f (expt.)
BrCdBr		80.90	−29.96	−30.96[86]
ClCdCl		91.14	−48.80	−45.60[86]
BrCdCl	90.60	81.36	−39.39	
BrCdO	65.03	78.09	16.77	
ClCdO	65.74	88.05	6.67	
HCdBr	87.66	69.36	4.80	
HCdCl	98.14	70.59	−5.24	

[a] Calculated from the reaction enthalpies in Table 5. See the text.

by 30−40 kcal/mol, while the analogous cadmium reactions are only endothermic by 10−20 kcal/mol. Similarly, the enthalpies of the cadmium abstraction reactions involving BrO and ClO are 15−20 kcal/mol smaller than their mercury counterparts. High-level ab initio calculations on the global potential energy surface of Hg + Br_2 have shown that the abstraction reactions proceed without a barrier,[3] and this is presumably also the case for cadmium.

The cadmium-halide reactions are also similar to the mercury cases in that all of the processes forming insertion complexes are strongly exothermic. However, following the same trend as the abstraction reactions, the cadmium insertion reactions are all 25−30 kcal/mol more exothermic than the analogous mercury cases. Large potential energy barriers have been previously calculated for the insertion of mercury into BrO and Br_2,[3] i.e., the barrier height for Hg + Br_2 is 27.2 kcal/mol.[3] It is likely that there are also barriers to insertion in the cadmium reactions, but the stronger exothermicity may result in significantly lower values.

Finally, Table 6 lists the bond dissociation energies and 0 K heats of formation for the seven triatomic cadmium molecules. The heats of formation were calculated using the insertion reaction enthalpies for each triatomic species along with accurate experimental heats of formation for Cd and the halide-containing diatomics. The 0 K heats of formation that were used were as follows: 28.20 ± 0.05 kcal/mol for Cd,[88,89] 28.18 ± 0.01 kcal/mol for Br,[90] 28.590 ± 0.001 kcal/mol for Cl,[90] 10.92 ± 0.03 kcal/mol for Br_2,[90] 5.24 ± 0.02 kcal/mol for BrCl (derived from the D_0 of Tellinghuisen[91]), 24.14 ± 0.03 kcal/mol for ClO,[92] 31.3 ± 0.1 kcal/mol for BrO (derived from the D_0 of Kim et al.[93]), −22.016 ± 0.004 kcal/mol for HCl,[94] and −6.805 ± 0.06 for HBr.[94] Of course, the resulting differences between the experimental and theoretical heats of formation of $CdBr_2$ and $CdCl_2$ shown in Table 6 are identical to those shown in Table 5 for the insertion reaction enthalpies. A value of ΔH_f for CdBrCl has been previously determined from mass spectrometry measurements, 0.4 ± 1 kcal/mol.[22] This is in substantial disagreement, however, with our presently predicted value (−39.4 kcal/mol) and does not seem reliable.

The DFT calculations of Liao et al.[31] have yielded bond energies for CdCl (48.2 kcal/mol), CdBr (39.4 kcal/mol), BrCd−Br (59.3 kcal/mol), and ClCd−Cl (68.5 kcal/mol). By comparison, the current calculations predict bond energies of 43.6 kcal/mol for CdCl, 34.2 kcal/mol for CdBr, 80.9 kcal/mol for BrCd−Br, and 91.1 kcal/mol for ClCd−Cl. Thus, the DFT results for CdCl and CdBr are reasonably close to the present values, with DFT overestimating the bond strengths by 5−6 kcal/mol. Their particular choice of DFT (Xα), however, underestimates the bond dissociation energies of the triatomics species by ~22 kcal/mol in both cases. The MR-SOCI dissociation energy of CdH from ref 83 (15.8 kcal/mol) slightly underestimates the current and experimental values by 0.8 and 0.9 kcal/mol, respectively, while four-component CCSD calculations[84] (18.2 kcal/mol) yielded a value that was slightly too large by about 0.4 kcal/mol.

IV. Conclusions

Accurate ab initio calculations have been carried out to determine the thermochemistry of reactions between cadmium and reactive halogen species, as well as to determine the structures and vibrational frequencies of all the species involved. The specific reactions that have been investigated are

$$\mathrm{Cd} + \mathrm{XY} \rightarrow \begin{cases} \mathrm{CdX} + \mathrm{Y} \\ \mathrm{CdY} + \mathrm{X} \\ \mathrm{XCdY} \end{cases}$$

where X = {Cl, Br} and Y = {H, O, Cl, Br}. The cadmium molecules that have been characterized include the diatomic species CdH, CdO, CdCl, and CdBr and the triatomics CdHCl, CdHBr, CdClO, CdBrO, $CdCl_2$, $CdBr_2$, and CdBrCl. All of the triatomic molecules have linear equilibrium geometries with Cd as the central atom.

Electron correlation has been treated with the CCSD(T) method with a series of correlation consistent basis sets that allowed for extrapolation to the complete basis set limit. Accurate relativistic pseudopotentials have been used on the Cd and Br atoms to account for the major scalar and spin−orbit relativistic effects. Additional calculations were carried out using the one-component all-electron DKH Hamiltonian to estimate the errors associated with the pseudopotential approximation, as well as to recover the effects due to scalar relativity on the H, O, and Cl atoms. Additive corrections for core−valence correlation and spin−orbit coupling were also incorporated into the final results.

It is expected that the dissociation and reaction enthalpies of this work have been calculated to within 1 kcal/mol. Experimental enthalpies currently exist for only four of the reactions in this study, and with the exception of Cd + HBr → CdH + Br and Cd + HCl → CdH + Cl, the currently calculated enthalpies are believed to be the most accurate to date. With the exception of CdH, the bond lengths for the molecules of this study agree to within ±0.005 Å with the experimental values where they are available. With this one exception, the predicted equilibrium geometries for the cadmium-containing molecules are the most reliable values currently available and are expected to be accurate to within ±0.005 Å.

The enthalpies in the present study are qualitatively similar to previous calculations involving mercury and reactive halogen species. All of the abstraction reactions considered are endothermic, while the insertion reactions are strongly exothermic. The abstraction reactions involving cadmium, however, are several kcal/mol less endothermic than the corresponding mercury reactions, while the cadmium insertion reactions are more exothermic than their mercury counterparts. The mercury abstraction reactions are known to proceed without a barrier, while the insertion reactions have relatively large barriers. It is probable that the cadmium reactions follow this same trend.

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