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Heats of Formation of CBr, CHBr, and CBr_2 from Ab Initio Quantum Chemistry

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High-level ab initio electronic structure theory has been used to calculate the heats of formation of CBr, CHBr, and CBr_2. The calculations were done at the CCSD(T) level with correlation-consistent basis sets up through augmented quintuple-z and were extrapolated to the complete basis set limit. Additional corrections for core/valence correlation, relativistic effects both scalar and spin−orbit, and zero-point energies have been included. The heat of formation at 0 K of CBr ($^2\Pi$) is 119.92 ± 0.5 kcal/mol, of CHBr ($^1A'$) is 92.34 ± 0.7 kcal/mol, and of CBr_2 ($^1A_1$) is 86.92 ± 0.7 kcal/mol.

Introduction

We have been developing a composite theoretical approach to predict molecular heats of formation reliably without recourse to empirical parameters.[1−13] Our approach starts with existing, reliable thermodynamic values obtained from either experiment or theory. We use experimental atomic heats of formation, which are difficult to obtain theoretically, as well as molecular and atomic spin−orbit splittings (if available). High-level ab initio electronic structure methods are then used to calculate the molecular atomization energy. The energy of the valence electrons is calculated by using coupled cluster methods including single, double, and connected triple excitations (CCSD(T)), with the latter being handled perturbatively.[14−16] The CCSD(T) energies are extrapolated to the complete basis set (CBS) limit by using the correlation consistent basis sets (cc-pV*n*Z) from Dunning and co-workers.[17−20] This family of basis sets is chosen because of the regularity with which it approaches the CBS limit. In addition, core−valence (ΔE_{CV}) and relativistic, including both spin−orbit and scalar relativistic, corrections to the dissociation energy are required for <1 kcal/mol accuracy. Finally, one needs an accurate zero-point energy to calculate ΣD_0 at 0 K and hence ΔH_f at 0 K, given the atomic heats of formation.

The heats of formation of simple bromine-substituted carbon systems are important in terms of atmospheric chemistry because of the release of brominated compounds from fire-fighting systems (halons) as well as from fumigants (CH_3Br).[21,22] Brominated compounds can have a serious impact on the destruction of stratospheric ozone, as they are far more reactive in the ozone cycle as compared to the reactivity of chlorine. In addition, brominated compounds play a key role in combustion chemistry because of their use as fire-extinguishing compounds. One particular organobromine compound that is receiving attention is bromoform ($CHBr_3$), the main source of which is believed to originate from various forms of marine algae[23,24] and photoplankton.[25] Recently, Dvortsov et al.[26] found that bromoform alone in the stratosphere contributes more inorganic bromine than do the combined sources of all halons and methyl bromide. Photodissociation of bromoform is considered to be the main atmospheric removal mechanism. There have been two previous photodissociation studies of bromoform.[27,28] The photolysis studies show that the primary dissociation process is the loss of a bromine atom followed by secondary dissociation pathways to produce the CHBr and CBr radical species. Accurate knowledge of the heats of formation of CBr, CHBr, and CBr_2 is required to analyze results from the photodissociation studies.

We recently demonstrated that the heats of formation of CCl and CCl_2 at 0 K can be reliably calculated using the quantum chemical approach described above.[13] There have been a number of recent experimental measurements and calculations of the heat of formation of CBr_2. The experimental values are based on thermochemical cycles derived from Fourier transform ion cyclotron resonance experiments on selected anions. The heat of formation at 298 K of CBr_2 is given as ∼77.4 kcal/mol,[29] and that of CHBr is given as 89.1 ± 4.3 kcal/mol.[30] A recent table gives 80.4 ± 12 kcal/mol for CBr_2,[31] and the JANAF tables report a value of 123 ± 15 kcal/mol at 0 K and 122 ± 15 kcal/mol at 298 K for CBr.[32] Recent theoretical values for CBr_2 and CHBr include G2[33] and QCISD(T)[34] values at 298 K based on an isodesmic reaction approach yielding 80.3(81.0) and 88.7(90.8) kcal/mol, respectively, at the G2(QCISD(T)) level.[35] Another recent theoretical study on CBr_2 based on a reaction energy approach using CCSD(T) and the correlation-consistent basis sets led to a value of 80.5 ± 1.9 kcal/mol at 298 K.[36] In addition, G2 and QCISD(T) values at 298 K based on an isodesmic reaction approach average to 118.7 kcal/mol for ΔH_f(CBr) at 298 K, and the G2 value is 118.8 kcal/mol.[37]

Computational Approach

For the present study, we used the augmented correlation consistent basis sets aug-cc-pV*n*Z for C, H, and Br (n = D through 5). Only the spherical components (5-*d*, 7-*f*, 9-*g*, and 11-*h*) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.[38] The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level, where a restricted open-shell

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Hartree–Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[39–41] The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

where $n = 2$ (DZ), 3 (TZ), and 4(QZ), as first proposed by Peterson et al.[42] This extrapolation method has been shown to be the most appropriate method for extrapolations up through $n = 4$. In addition, extrapolations of the CCSD(T) energies for $n = 4$ and 5 were also performed with the two-parameter function[43,44]

$$E(n) = E_{\mathrm{CBS}} + A l_{\max}{}^{-3} \quad (2)$$

where $l_{\max}$ is the highest l value in the basis set and is equal to n. The CBS-limit total energy was obtained by averaging the values from eqs 1 and 2. The spread between the CBS values obtained via eqs 1 and 2 was used to estimate the uncertainty in the extrapolations.

The geometries were optimized at the frozen core CCSD(T)/aug-cc-pV*nZ* levels of theory. For CBr, CHBr, and CBr_2, the geometries were obtained at n = D, T, and Q, whereas for CBr, the geometry was also obtained at $n = 5$. The frequencies for CHBr and CBr_2 were obtained at the n = T level. For CBr, the spectroscopic constants were calculated from a sixth-order polynomial fit to seven near-equilibrium energies at the CCSD(T)/aug-cc-pV5Z level of theory.

ΔE_{CV} was obtained at the CCSD(T)/cc-pwCVTZ level of theory[45] from both valence-only correlated calculations and from those where correlation of the C 1s and Br 3s3p3d electrons was also included. As in most electronic structure calculations, the present work does not explicitly account for any zero-field spin–orbit splittings but instead yields a weighted average of the available multiplets. To correct for this effect, we apply an atomic spin–orbit correction of −0.08 kcal/mol for C and −3.51 kcal/mol for Br on the basis of the excitation energies of Moore.[46] For CBr, a molecular spin–orbit splitting of 468 cm^{-1} is available from experiment.[47] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the aug-cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass–velocity and one-electron Darwin (MVD) terms in the Breit–Pauli Hamiltonian.[48] In addition, we performed fully relativistic Dirac–Hartree–Fock calculations using the MOLFDIR program package[49] with aug-cc-pVTZ basis sets to assess the accuracy of the scalar relativistic MVD corrections.

Results and Discussion

The geometry results are shown in Table 1, and the vibrational frequencies are shown in Table 2. The calculations reported in these tables as well as the energetic results in Table 3 are for the ground states of CBr ($^2\Pi$), CHBr ($^1A'$), and CBr_2 ($^1A_1$). Our results for CBr_2 for the geometries and frequencies are in excellent agreement with the CCSD(T)/cc-pVTZ results previously reported.[36] The calculations are not in as good agreement with the spectroscopic results in an Ar matrix,[50] which gave R(CBr) = 1.865 Å and <BrCBr = 100.7°. The frequencies agree well with the experimental values of $\omega_1 = 599$,[51] $\nu_2 = 196$,[50,52] and $\nu_3 = 641$ cm^{-1}.[50,52]

TABLE 1: Geometry Parameters for CBr, CHBr, and CBr_2[a]

species	parameter	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	expt[c]
$^2\Pi$ CBr	R(CBr)	1.8535	1.8305	1.8257 (1.8231)[b]	1.81517
$^1A'$ CHBr	R(CH)	1.1270	1.1102	1.1088	1. 116(9)
	R(CBr)	1.8881	1.8666	1.8619	1.854(2)
	<HCBr	100.64	101.00	101.04	102.6(9)
$^3A''$ CHBr	R(CH)	1.0987	1.0836		
	R(CBr)	1.8403	1.8209		
	<HCBr	126.53	126.79		
$^1A_1$ CBr_2	R(CBr)	1.9182	1.8960	1.8912	1.865
	<BrCBr	109.95	110.04	109.90	100.7
$^3B_1$ CBr_2	R(CBr)	1.8578	1.8391		
	<BrCBr	128.84	129.17		

[a] Bond distances in angstroms and bond angles in degrees. [b] aug-cc-pV5Z optimized value. [c] CBr (ref 53); CHBr (ref 55); CBr_2 (ref 50).

TABLE 2: Vibrational Frequencies in cm^{-1} for CBr, CHBr, and CBr_2[a]

molecule	basis	ω_1	ω_2	ω_3
$^2\Pi$ CBr	aug-cc-pV5Z	731.5[b] (727.99)[c]		
$^1A'$ CHBr	aug-cc-pVTZ	2926.7	1156.2	682.4 (670 ± 20)[d] (694 ± 25)[d]
$^1A_1$ CBr_2	aug-cc-pVTZ	599.4 (A_1) (599)[e]	196.8 (A_1) (196)[f]	655.6 (B_1) (641)[f]
$^3A''$ CHBr	aug-cc-pVDZ	3175.0	913.1	731.0
$^3B_1$ CB_{r2}	aug-cc-pVDZ	526.8 (A_1)	178.8 (A_1)	849.1 (B_1)

[a] Experimental values are in parentheses. [b] The vibrational anharmonicity constant is 3.9 cm^{-1}. [c] Ref 47. [d] Ref 56. [e] Ref 51. [f] Refs 50 and 52.

The CBr radical has been the subject of recent microwave[53] and diode laser infrared spectroscopy studies.[47] Our CCSD(T)/aug-cc-pV5Z equilibrium bond length of 1.8231 Å is in very good agreement with the accurate experimental value of 1.81517 Å.[53] The remaining discrepancy is predominately due to the neglect of core–valence correlation and scalar relativity in the geometry optimization (cf. calculations[54] on the isoelectronic BBr^- molecule where both of these effects decreased the equilibrium bond length). The calculated harmonic frequency at the same level of theory (731.5 cm^{-1}) is also in excellent agreement with the experimentally derived value[47] of 727.99 cm^{-1}, as is the anharmonicity correction.

The CCSD(T)/aug-cc-pVQZ geometry of X^1A' CHBr shown in Table 1 is in good agreement with the experimental values[55] of R(CBr) = 1.854(2) Å, R(CH) = 1.116(9) Å, and <HCBr = 102.6(9)° obtained from high-resolution transient laser absorption spectroscopy of the vibrational ground state; the calculated value for R(CH) is within the experimental uncertainty, whereas as discussed above for CBr, R(CBr) is somewhat too long because of the neglect of both core–valence correlation and scalar relativity. Our result for the valence angle lies about 0.7° below the lower end of the experimental range, which could be due to comparing an equilibrium angle with its value in the vibrational ground state. The harmonic frequency calculated for the CBr stretch in CHBr (682.4 cm^{-1}) is in excellent agreement with the experimental values of $\omega_3 = 670 \pm 20$ cm^{-1} and $= 694 \pm 25$ cm^{-1}.[56] The calculated frequencies were used directly in the zero-point energy calculations, which will introduce a maximum error of 0.2 kcal/mol for CHBr where the presence of the light hydrogen atom is the largest potential source of error in this term.

The various components of the energy are shown in Table 3. The error bars for the valence electronic atomization energies are estimated as the difference between the results of eq 1 using

TABLE 3: Contributions to the Total Energy of C, Br, CBr, CHBr, and CBr_2 and Relative Energies

contribution[a]	C	Br	CBr	CHBr	CBr_2
aug-cc-pVDZ	−37.764803	−2572.485690	−2610.3658986	−2610.9949549	−5182.9480584
aug-cc-pVTZ	−37.781729	−2572.606199	−2610.5130033	−2611.1479862	−5183.2217215
aug-cc-pVQZ	−37.7867701	−2572.6231614	−2610.5384186	−2611.1746201	−5183.2666887
aug-cc-pV5Z	−37.7882673	−2572.6283198	−2610.5463134	−2611.1828272	−5183.2896692
estimated CBS, eq 1[b]	−37.789598	−2572.630438	−2610.550489	−2611.187278	−5183.287579
estimated CBS, eq 2[c]	−37.789381	−2572.633732	−2610.554591	−2611.191438	−5183.295337
E_{CV}[d]	−0.048264	−0.693728	−0.741272	−0.741483	−1.4357111
E_{SR}[e]	−0.0149461	−31.1276852	−31.1418113	−31.1414989	−62.2684998
ΔE_{elec} CBS, eq 1			81.86	167.69	148.78
ΔE_{elec} CBS, eq 2			82.20	168.08	149.37
ΔE_{elec} CBS			82.03 ± 0.2	167.88 ± 0.2	149.08 ± 0.3
ΔE_{CV}			0.45	0.32	0.00
ΔE_{SR}			−0.27	−0.47	−0.49
ΔE_{SO}[f]			−2.92	−3.59	−7.10
ΔE_{ZPE}[g]			−1.05	−6.69 ± 0.2	−2.07
ΣD_0[h]			78.24 ± 0.4	157.45 ± 0.6	139.42 ± 0.6
ΔH_f (0 K)			119.92 ± 0.5	92.34 ± 0.7	86.92 ± 0.7
ΔH_f (298 K), calc			119.1 ± 0.5	90.50 ± 0.7	83.71 ± 0.7
ΔH_f (298 K), expt			122 ± 15[32]	89.1 ± 4.3[30]	77.4[29] 80.4 ± 12[31]
ΔH_f (298 K), calc			118.8[37] 118.7[37]	88.7[35] 90.8[35]	80.3[35] 81.0[35] 80.5 ± 1.9[36]

[a] Total energies in Hartrees and energy differences in kcal/mol. The final estimated uncertainties in ΣD_0 and ΔH_f do not include the intrinsic errors of the CCSD(T) method. [b] Estimated frozen core, complete basis set energies obtained from eq 1 using the CCSD(T)/aug-cc-pVxZ (x = D, T, Q) energies. [c] Estimated frozen core, complete basis set energies obtained from eq 2 using the CCSD(T)/aug-cc-pVxZ (x = Q,5) energies. [d] Core/valence corrections were obtained from R/UCCSD(T)/cc-CVQZ calculations. [e] Scalar relativistic corrections were obtained from CI/aug-cc-pVTZ MVD calculations. [f] Net spin−orbit correction to the atomization energy. For CBr, correction of (466/2) cm^{-1} is included. [g] Contributions from the zero-point vibrational energies of CBr, CHBr, and CBr_2. [h] $\Sigma D_0 = \Delta E_{elec} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPE}$.

the DZ through QZ basis sets and eq 2 using the QZ and 5Z sets, the error in the relativistic correction, and the error in the zero-point energy, which yields error limits of ±0.4 kcal/mol for CBr, ±0.6 kcal/mol for CHBr, and ± 0.6 kcal/mol for CBr_2. By combining our computed ΣD_0 values with the known[32] heats of formation at 0 K for the elements ($\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal/mol, $\Delta H_f^0(H) = 51.63$ kcal/mol, and $\Delta H_f^0(Br) = 28.18 \pm 0.001$ kcal/mol), we derive ΔH_f^0 values for CBr, CHBr, and CBr_2 as shown in Table 3. We convert the ΔH_f values to 298 K by using the procedures of Curtiss et al.[57] The heat of formation of CBr at 0 K is 119.9 ± 0.5 kcal/mol, and at 298 K, it is 119.1 ± 0.5 kcal/mol (including the correction for the spin−orbit splitting of the CBr ground state of 468 cm^{-1})[47] as compared to experimental values[32] of 123 ± 15 and 122 ± 15 kcal/mol at 0 and 298 K, respectively. Clearly, our value for ΔH_f(CBr) is the most reliable available value, although we note that the estimated experimental value is reasonable. Our calculated value for ΔH_f(CBr) at 298 K is in good agreement with the G2 value of 118.8 kcal/mol even though spin−orbit corrections for the atoms are not included. Isodesmic reactions at the G2 level or at the QCISD(T)/6-311+G(3df, 2p) level average to 118.7 kcal/mol for ΔH_f(CBr) at 298 K.[37] For ΔH_f(CHBr), our calculated value of 90.5 ± 0.7 kcal/mol at 298 K is in good agreement with the experimental value[30] of 89.1 ± 4.3 kcal/mol and with an available theoretical value[35] of 88.7 kcal/mol from G2 isodesmic reactions as well as from QCISD(T)/6-311+G(3df,2p) isodesmic reaction energies, which give a value of 90.8 kcal/mol. Our result for $\Delta H_f(CBr_2)$ of 83.7 ± 0.7 kcal/mol at 298 K is larger in magnitude than the experimental value[29] of 77.4 kcal/mol from ion−molecule reaction measurements. It is also larger than the value of 80.5 ± 1.9 kcal/mol reported by Sendt and Bacskay[36] who calculated this value at a variety of levels using the reactions of CH_2, CF_2, and CCl_2 with Br_2 to form CBr_2 and H_2, F_2, and Cl_2, respectively. Our calculated value is also larger than the result of 80.3 kcal/mol calculated at the G2 level from an isodesmic reaction scheme as well as a value of 81.0 kcal/mol from QCISD(T)/6-311+G(3df,2p) isodesmic reaction energies.[35] We feel that our calculated results are the most reliable values available for the heats of formation of these compounds.

The scalar relativistic calculations are somewhat dependent on the level of the calculation. At the Hartree−Fock level, the relativistic corrections are −0.50, −0.71, and −1.09 kcal/mol as compared to the CI-SD values of −0.27, −0.47, and −0.49 kcal/mol for CBr, CHBr, and CBr_2, respectively. At the fully relativistic aug-cc-pVTZ Dirac−Hartree−Fock level, the total relativistic corrections are −3.57, −4.35, and −8.09 kcal/mol for these three systems. Accounting for the (calculated) spin−orbit splitting, the scalar relativistic corrections are found to be −0.47, −0.66, and −0.83 kcal/mol. The scalar relativistic corrections obtained from Hartree−Fock with MVD are in good agreement with the fully relativistic results. The correlation effects from the CI-SD calculations are in line with earlier fully relativistic benchmark calculations on the various halide species.[58−60] On the basis of the differences between the MVD and fully relativistic Hartree−Fock results, we assign an estimated uncertainty of ±0.2 kcal/mol to the scalar relativistic correction in Table 3.

One issue that has been raised is the size of the singlet−triplet splittings in CHBr and CBr_2. We optimized the geometries of the lowest triplet state for these compounds at the CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The geometry parameters are given in Table 1. We used the CCSD(T)/aug-cc-pVTZ geometry to calculate the energy at the CCSD(T)/aug-cc-pVQZ level and then used these energies to extrapolate to the complete basis-set limit. The various energy components are given in Table 4. These values were used to calculate the singlet−triplet splittings given in Table 4. The singlets are more stable than the triplets by 5.35 kcal/mol for CHBr and 15.97 kcal/mol for CBr_2. The zero-point differences are on the order of 0.1−0.2 kcal/mol and are not included in these values. These results are in reasonable agreement with

TABLE 4: Contributions in Atomic Units to the Total Energies $^3A''$ CHBr and $^3B_1$ CBr$_2$

contribution[a]	^{3}CHBr	^{3}CBr$_2$
aug-cc-pVDZ	−2610.9866014	−5182.9221671
aug-cc-pVTZ	−2611.1399177	−5183.1966511
aug-cc-pVQZ	−2611.1662629	−5183.2414060
estimated CBS, eq 1[b]	−2611.178746	−5183.262124
ΔE ($S - T$), kcal/mol[c]	5.35	15.97

[a] CCSD(T) total energy at a given basis set in a.u. [b] Estimated frozen core, complete basis set energies obtained from eq 1 using the CCSD(T)/aug-cc-pVxZ (x = D, T, Q) energies. [c] Singlet−triplet splitting in kcal/mol.

the values[35] of 4.8 kcal/mol (HCBr) and 15.1 kcal/mol (CBr$_2$) calculated at the QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G-(d,p) level as well as the value of 16.59 kcal/mol (CBr$_2$) calculated at the CCSD(T)/cc-pVQZ level.[36] Our calculated value for the singlet−triplet splitting in CHBr is just above the upper limit of 2.6 ± 2.2 kcal/mol obtained from photodetachment experiments.[56]

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