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Thermodynamic Properties of C_1 and C_2 Bromo Compounds and Radicals. A Relativistic ab Initio Study

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Heats of formation for a number of key C_1 and C_2 bromoalkanes and radicals have been calculated ab initio, both directly using an all-relativistic variant of W2 theory and indirectly using Douglas−Kroll relativistic CCSD(T)/Aug-VTZ reaction energies. For some of the bromoalkanes, our calculated values represent the first reliable data available. Bromine (3d) correlation contributes significantly to the molecular binding energies, but the effect of bromine (3s, 3p) correlation appears to be very small despite these orbitals lying above the carbon (1s) in energy. Thermodynamic functions have been obtained from molecular geometries and harmonic frequencies obtained at the B97-1/Aug-VTZ level and are given in the Supporting Information. These accurate thermodynamic parameters can be used to develop kinetic rate parameters.

Introduction

There has been an increasing interest in the thermal decomposition and reactions of brominated hydrocarbons (BHCs) due to their role in fire suppression as well as their potential to form a variety of environmental pollutants.[1−4] The decomposition of halons, such as CF_3Br, result in the release of halogens that can scavenge hydrogen atoms and prevent flame propagation.[5] Surprisingly, significant quantities of BHCs have also been observed in the effluent of hazardous and municipal waste incinerators as well as other combustion/thermal sources.[1] The emissions of small C_1 and C_2 BHCs are of health concern in their own right.[6]

The reported studies on the thermal degradation of halons have focused on their fire suppression properties and their ability to scavenge chain propagating radicals.[4] Work on the kinetics of brominated compounds has been hampered by the imprecise and conflicting character of the available thermodynamic data. For example, the measured heat of formation for even a simple molecule such as CBr_4 varies greatly between different sources (12.00,[7] 18.8,[8] 20.1,[9] and 35.13[10] kcal/mol). Thus, the evaluation of the thermochemistry of BHC species in a reliable manner is of a very high priority.

Traditionally, when reliable experimental thermochemical data are not available, researchers rely on estimation methods. Benson's group additivity method[11] is commonly preferred and has been found to be far more reliable than any other estimates. However, even this method does not yield uniform results. There are disputes among researchers regarding specific values for some of the group equivalents, especially those including atoms other than C and H. Group data involving bromine are totally missing or of questionable validity. Moreover, as already stated, the limited experimental data are highly inaccurate.

In this work, we will attempt to accurately determine the heats of formation of these problematic species by three different ab initio (-based) approaches. The first, direct, approach is an all-relativistic variant of W2 theory,[12] which has been demonstrated to usually yield results in the subkilocalorie per mole (often kilojoule per mole) accuracy range.[13] As W2 theory is computationally too demanding for species with four to six bromine atoms, we determined the heats of formation of the other species indirectly through isogyric and isodesmic reaction energies. The latter were calculated by means of relativistic coupled cluster methods; density functional theory (DFT) was used for the reference geometries, zero-point vibrational energies, and thermal corrections. For comparison, we also consider results from the widely used and fairly inexpensive G2 thermochemistry scheme.[14,15]

Computational Details

All calculations were performed using GAUSSIAN 03[16] or MOLPRO 2002[17] as appropriate. All coupled cluster calculations were carried out using MOLPRO, while all density functional theory and G2 theory calculations were performed using Gaussian 03.

The basis sets employed in the DFT and coupled cluster calculations are new relativistic correlation consistent basis sets developed at Weizmann.[18] These basis sets include VTZ (valence triple-ζ), VQZ (valence quadruple-ζ), and V5Z (valence quintuple-ζ) basis sets, which are of *spdf*, *spdfg*, and *spdfgh* quality, respectively, as well as variants augmented with a single diffuse function of each angular momentum (Aug-VTZ, Aug-VQZ, and Aug-V5Z) and variants including core correlation functions (CVTZ, CVQZ, CV5Z). These basis sets were all optimized and contracted for relativistic energies within the Douglas−Kroll (DK)[19] (no-pair) approximation.

To save computer time, geometry optimizations and vibrational frequency calculations were carried out by means of density functional theory (DFT) using the B97-1 hybrid DFT exchange-correlation functional[20] with the Aug-VTZ basis set. It has been shown[21] that such a basis set yields results very close to the basis set limit for a DFT calculation, and that the B97-1 functional yields the best overall performance for the

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TABLE 1: Enthalpies of Formation of Some C_1 and C_2 Brominated and Chlorinated Molecules and Radicals

bromo species	new $\Delta_f H_{298}$,[c] kcal/mol	old $\Delta_f H_{298}$,[d] kcal/mol	ref	chloro species	$\Delta_f H_{298}$,[d] kcal/mol	ref
$CHBr_3$	12.97	13.24 ± 0.79	29	$CHCl_3$	−24.52 ± 0.6	30
$CHBr_2$	47.44	44.98 ± 2.2	31	$CHCl_2$	17.66	32
$CHBr$	90.31	83.15 ± 4.3	33	$CHCl$	73.68	32
CBr_4	28.49	20.05 ± 0.8	9	CCl_4	−22.85 ± 0.6	30
CBr_3	55.50	49.50 ± 1.9	34	CCl_3	17 ± 1.2	35, 40
CBr_2	82.10	84.3	36	CCl_2	57 ± 5	29
CBr	118.51	122.0	29	CCl	120	29
C_2HBr	67.50	64.3 ± 1.5	37	C_2HCl	54.11 ± 2.4	30
C_2HBr_2[a] cis, trans	81.60, 83.91	80.59	40	C_2HCl_2 cis + trans	60.2	38[b]
C_2HBr_3	34.46	19.37 ± 2	40	C_2HCl_3	−4.18 ± 0.7	30
$CHBr_2CBr_2$	52.30	32.88 ± 6	40	C_2HCl_4	9.58 ± 2.0	32
C_2HBr_5	27.03	−11.62	40	C_2HCl_5	−37.26 ± 1	30
C_2Br	149.06	126.6	72	C_2Cl	118.09	29
C_2Br_2	80.14	47.19 ± 2	39, 40	C_2Cl_2	54.15 ± 3.3	30
C_2Br_3	92.11	75.61	40	C_2Cl_3	45.48	32
C_2Br_4	45.43	14.4 ± 2	39, 40	C_2Cl_4	−5.78 ± 1	30
C_2Br_5	67.70	102	40	C_2Cl_5	9.32	32
C_2Br_6	39.55	31.79	34	C_2Cl_6	−35.42 ± 1.4	30

[a] $\Delta_f H_{298} = 89.18$ kcal/mol for the gem configuration. [b] Value of $\Delta_f H_0 = 54.1$ kcal/mol from ref 38 assuming an equal mixture of cis and trans CHCl = CCl, $\Delta_f H_0$ (C_2HCl_3) = −3.3 ± 0.7 kcal/mol[30] and $\Delta_f H_0$ (Cl) = 28.59 ± 0.002 kcal/mol.[7] For the gem configuration $\Delta_f H_0 = 70.$ kcal/mol. [c] This work. [d] Literature.

properties of interest. Zero-point and thermal corrections within the rigid rotor-harmonic oscillator approximation were obtained from rotational constants and harmonic frequencies at this level of theory. (For some individual molecules, calculations using the older, but very widely used, B3LYP functional[22] were also performed.)

Benchmark calculations on the smaller species were performed using a fully relativistic variant of the W2 method (denoted W2DK throughout the paper), at the B97-1/Aug-VTZ reference geometries. (In standard W2 theory, relativistic corrections are calculated separately and added to an otherwise nonrelativistic results: this is acceptable in the first and second rows of the periodic table but may be questionable for heavy-element systems.) The total atomization energies of these species were separated into their individual components and calculated as follows.

1. The SCF (self-consistent field) component of the energy was extrapolated from relativistic (DK) Aug-VQZ and Aug-V5Z calculations using the formula first proposed by Halkier et al.:[23]

$$E_\infty = E_n + \frac{E_n - E_{n-1}}{(n/(n-1))^\beta - 1} \qquad (1)$$

where n is the cardinal number of the larger VnZ basis set and $\beta = 5$ as in W2 theory.[24] The high exponent reflects the relatively fast convergence of the SCF component.

2. The CCSD (coupled cluster with all single and double substitutions) component was extrapolated using eq 1 but with $\beta = 3$, thus rendering the leading term in the asymptotic partial wave expansion of singlet-coupled pair correlation energies.[25] The CCSD(T) − CCSD difference, i.e., the contribution of quasiperturbative connected triple excitations,[26] was likewise extrapolated from the Aug-VTZ and Aug-VQZ calculations.

3. Atomic spin−orbit corrections were taken from the Supporting Information to Martin and Sundermann;[27] the spin−orbit splittings of CBr and BrO were taken from Huber and Herzberg.[28]

4. The contribution of 3d correlation for the bromine atoms was calculated using Aug-CVTZ and Aug-CVQZ basis sets (obtained by adding the diffuse functions of the Aug-VnZ basis sets to the CVnZ sets), and extrapolated using eq 1 with β = 3.22 as in the original W1 theory.[12] (The increased exponent compensates for "overshooting" with extrapolations from lower-angular momentum basis sets, cf. ref 12.) The 3d contribution was computed as the difference between a valence CCSD(T) calculation (correlating 4s4p orbitals on bromine, 2s2p on carbon and 1s on hydrogen) and a "relaxed inner valence" calculation (correlating 3d4s4p on Br, 2s2p on C, and 1s on H).

5. The contribution of carbon (1s) inner-shell and bromine (3s3p) deep-core correlation was computed with CVTZ basis sets. (It is impossible to treat carbon (1s) correlation separately as the carbon (1s) orbitals are below the bromine (3s, 3p) orbitals in energy.) This was taken as the difference between two CCSD(T) calculations: one correlating the 3d4s4p orbitals of bromine, 2s2p orbitals of carbon and 1s of hydrogen, and the other correlating 3s3p3d4s4p on Br, 1s2s2p on C and 1s on H. For reasons of computational cost, we were unable to employ larger basis sets for this contribution.

Similar calculations were performed for tetrabromomethane (CBr_4), but at a lower level of theory due to the high computational cost. SCF and CCSD(T) components were extrapolated from Aug-VTZ and Aug-VQZ (again using the 3.22 exponent). Correlation of 3d orbitals was calculated only with Aug-CVTZ basis sets. We were unable to compute the C(1s) and Br(3s,3p) contribution in this case, but have reason to believe it is very small (see Results and Discussion).

The energies of the molecular components of heats of formation based on isogyric and isodesmic reactions (vide infra) were calculated at the DK-CCSD(T)/Aug-VTZ level. This level of theory is insufficient for calculating total atomization energies because of the large change in electron correlation. Nonetheless, it should suffice for accurately calculating isodesmic (and possibly isogyric) reaction energies.

Heats of formation were also calculated using the relatively inexpensive G2 computational thermochemistry protocol as implemented in GAUSSIAN 03.[16] G2 theory[14] combines basis set additivity steps at second- and fourth-order in perturbation theory (MP2 and MP4) with basis sets no more extended than *spdf* (i.e., 6-311G(2df,p)), with MP2/6-31G* reference geometries and SCF-level vibrational frequencies. The appreciable remaining basis set incompleteness is supposedly absorbed by an additive empirical "high level correction" that is part of the method. G2 theory accounts for neither subvalence correlation nor scalar relativistic effects, although inclusion of atomic spin−orbit splitting has been recommended for third-row atoms.[15] We have followed this recommendation.

Thermochemical Calculations

The enthalpies of formation of all the brominated species calculated in this study are listed in Table 1 and compared with the older estimates used until recently in a thermochemical compilation[40] and the values for their chlorinated counterparts.

Heats of Formation from W2-type Calculations. A few compounds were chosen as "test subjects" for in-depth investigation: bromomethane (CH_3Br), dibromomethane (CH_2Br_2), bromomethylidene (CBr), dibromomethylene (CBr_2), bromoacetynyl radical (C_2Br), bromoacetylene (C_2HBr), and dibromoacetylene (C_2Br_2). The different contributions to the total atomization energy (TAE, i.e., the energy required to break up a molecule in all its constituent atoms in their respective ground states) are listed in Table 2. The standard heats of formation at room temperature $\Delta_f H°(298K)$ were calculated according to eqs 2−4,[13] where ZPVE is the zero-point vibrational energy and hcf_{298} denotes the heat capacity function (enthalpy correction) $H_{298} - E_0$. Table 3 lists the enthalpies of formation determined using the various different methods. The agreement of the W2DK enthalpies of formation with the previously reported values is poor (except for CH_3Br). This, however, probably reflects the large variations in the empirical data and their quality (vide supra), clearly demonstrating the need for reliable computational data.

$$\mathrm{TAE}_0 = \mathrm{TAE}_e + \mathrm{ZPVE} \qquad (2)$$

$$\Delta_f H°(C_xH_yBr_z, 0\ K) = x\Delta_f H°(C, 0\ K) + y\Delta_f H°(H, 0\ K) + z\Delta_f H°(Br, 0\ K) - \mathrm{TAE}_0(C_xH_yBr_z, 0\ K) \qquad (3)$$

$$\Delta_f H°(C_xH_yBr_z, 298\ K) = \Delta_f H°(C_xH_yBr_z, 0\ K) + hcf_{298}(C_xH_yBr_z) - x\ hcf_{298}(C, gr) - {}^1/_2 y\ hcf_{298}(H_2, g) - {}^1/_2 z\ hcf_{298}(Br_2, g) \qquad (4)$$

Heats of Formation via Isogyric and Isodesmic Reactions. The size of the brominated species of interest (particularly the number of electrons to be correlated in the inner-shell steps) precludes an investigation of the entire set using W2DK theory. However, isogyric reactions, in which the total number of unpaired electron spins is preserved,[48] constitute a cost-effective alternative. Rather than calculate the total atomization energy of, e.g., $CHBr_3$ directly via the reaction

$$CHBr_3 \rightarrow C + H + 3Br \qquad (5)$$

one can calculate the enthalpy change of the isogyric reaction

$$CHBr_3 + 3H_2 \rightarrow CH_4 + 3HBr \qquad (6)$$

This can be obtained with reasonably accuracy even at the CCSD(T)/Aug-VTZ level. This is evident from Table 4, which compares the convergence behavior of total atomization energies (Table 2) and the energy changes in some isogyric reactions (Table 5). Using the reaction enthalpies and the known heats of formation of CH_4, H_2 and HBr (vide infra), a reliable estimate of $\Delta_f H°(298\ K)$ of $CHBr_3$ can, in principle, be calculated.

The isogyric reactions used in this work all correspond to the general formula

$$C_xH_yBr_z + zH_2 \rightarrow C_xH_{y+z} + zHBr \qquad (7)$$

TABLE 2: Components of the Total Atomization Energies (TAE_e, kcal/mol) of Brominated Compounds[a]

	SCF[b]	CCSD[b]	(T)[b]	3d corr[c]	deep core[d]
CBr (Spin−Orbit Correction = −2.93)[e]					
TZ	40.12	32.67	5.49	0.82	0.03
QZ	40.44	34.21	5.71	0.72	
5Z	40.45	34.85	5.80		
extrap (TQ)	40.53	35.22	5.85	0.65	
extrap (Q5)	40.46	35.51	5.90		
CH_2Br_2 (Spin−Orbit Correction = −7.11)[e]					
TZ	247.20	83.47	7.70	1.47	0.65
QZ	247.73	86.90	8.06	1.41	
5Z	247.83	88.14	8.20		
extrap (TQ)	247.90	89.14	8.29	1.37	
extrap (Q5)	247.87	89.45	3.34		
C_2Br (Spin−Orbit Correction = −3.68)[e]					
TZ	137.02	68.91	10.12	0.76	1.23
QZ	129.94	80.19	10.54	0.59	
5Z	129.53	81.95	10.70		
extrap (TQ)	127.73	87.58	10.82	0.48	
extrap (Q5)	129.33	83.80	10.87		
C_2HBr (Spin−Orbit Correction = −3.68)[e]					
TZ	253.27	90.19	10.34	0.74	1.89
QZ	254.17	94.71	10.78	0.61	
5Z	254.36	96.24	10.95		
extrap (TQ)	254.45	97.68	11.07	0.53	
extrap (Q5)	254.45	97.85	11.12		
CBr_2 (Spin−Orbit Correction = −7.11)[e]					
TZ	73.09	59.04	10.42	1.62	0.00
QZ	73.59	61.76	10.86	1.46	
5Z	73.62	62.86	11.03		
extrap (TQ)	73.74	63.54	11.14	1.35	
extrap (Q5)	73.63	64.01	11.22		
CH_3Br (Spin−Orbit Correction = −3.60)[e]					
TZ	291.47	80.47	4.85	0.72	0.82
QZ	291.90	83.63	5.08	0.70	
5Z	292.00	84.65	5.17		
extrap (TQ)	292.03	85.70	5.23	0.69	
extrap (Q5)	292.05	85.72	5.26		
C_2Br_2 (Spin−Orbit Correction = −7.19)[e]					
TZ	206.91	92.95	13.10	1.44	1.91
QZ	208.09	97.70	13.66	1.19	
5Z	208.31	99.50	13.88		
extrap (TQ)	208.46	100.82	14.03	1.02	
extrap (Q5)	208.42	101.39	14.11		
CBr_4 (Spin−Orbit Correction = −14.05)[e]					
TZ	247.20	83.47	7.70	3.12	[0.0][f]
QZ	247.73	86.90	8.06		
extrap (TQ)	247.90	89.14	8.29		

[a] Douglas-Kroll relativistic approximation used throughout. [b] SCF, CCSD and (T) calculations performed with the AV*n*Z basis sets. [c] 3d contribution to correlation energy calculated with the ACV*n*Z basis sets. [d] Deep-core contribution to the correlation energy calculated with the CV*n*Z basis sets. [e] Spin−orbit splittings were taken from refs 27 and 28 (see text). [f] Could not be calculated with available hardware but expected to be very small from consideration of CBr and CBr_2 (see text).

Reaction energies were calculated for each of the isogyric reactions using the formula:

$$\Delta E_e(\mathrm{react}) = E_{\mathrm{CCSD(T)/AVTZ}}(C_xH_{y+z}) + zE_{\mathrm{CCSD(T)/AVTZ}}(HBr) - E_{\mathrm{CCSD(T)/AVTZ}}(C_xH_yBr_z) - zE_{\mathrm{CCSD(T)/AVTZ}}(H_2) \qquad (8)$$

The changes in zero-point vibrational energies (ΔZPVE) and

TABLE 3: Computed and Experimental Enthalpies of Formation ($\Delta_f H^0$(298 K), kcal/mol) of C_1 and C_2 Molecules and Radicals Containing Bromine

compound	W2DK	isogyric[i]	isodesmic[i]	G2	exptl	ref	prev calcd	ref
CBr	118.51	119.93	119.08	119.08	122.0 ± 15.1	41[a]	119.55	42
CBr_2	82.10	83.24	82.98	81.23	80.4 ± 12.0	41[b]	85.35	42
					84.4 ± 7.2	10	80.5 ± 2	43
CBr_3		56.20	55.50	56.64	42.1	8	55.36 ± 0.7	44
					49.5 ± 1.9	34		
					64.8 ± 7.2	10		
CBr_4	28.49[c]	28.75	28.22	28.52	12.00	7	25.23 ± 0.8	44
					18.9	8		
					20.1 ± 0.81	9		
					35.1	10		
CHBr		90.44	90.31	89.02	81.3 ± 4.7	40[d]	91.23	42
					89.15 ± 4.3	33	90.5 ± 0.7	47
$CHBr_2$		47.70	47.44	48.57	45.00 ± 2.15	45	47.06	42
					54.3	40	48.11 ± 0.6	44
$CHBr_3$		13.36	12.97[d]	13.93	4.06	8	5.69	46
					13.2 ± 0.79	9	12.16 ± 0.7	44
CH_2Br_2	1.18	1.40	1.14	2.17	−2.61 ± 2.15	45	0.60	42
					2.62	33	1.07 ± 0.6	44
CH_3Br	−8.71	−8.58	–	−8.09	−8.2 ± 0.2	9[e]	−9.56	42
					−8.97 ± 0.35	9[f]	−8.8	52
					−9.0 ± 0.32	9[f]		
C_2Br[g]	149.06[h]	149.40	149.27		126.6	40		
C_2Br_2	80.14[h]	79.99	79.73	79.98	47.16	40		
					61.8	40		
C_2Br_3		92.50	92.11		75.61	40		
C_2Br_4		45.95	45.43	45.79	14.4	40		
C_2Br_5		68.26	67.70		102.	40		
C_2Br_6		40.33	39.55	40.71	31.8	9		
C_2HBr	67.50[h]	67.04	66.91	68.25	64.2 ± 1.5	9		
C_2HBr_2 (cis)		81.86	81.60	83.73	80.59	40		
C_2HBr_2 (trans)		84.17	83.91	85.98				
C_2HBr_2 (gem)		87.03	86.77	89.18				
C_2HBr_3		34.85	34.46	35.19	19.37	40		
CBr_3CHBr		58.75	58.23					
$CHBr_2CBr_2$		52.82	52.30					
C_2HBr_5		28.03	27.03		−11.62	40		

[a] Best previous calculation: 119.1 ± 0.5 kcal/mol.[47] [b] Best previous calculation: 83.7 ± 0.1 kcal/mol.[47] [c] Direct calculations for CBr_4 were performed at a lower level of theory than for the other systems; see text for details. [d] $\Delta_f H°$ of $CHBr_3$ calculated from the isodesmic reaction $CHBr_3 + CH_3Br \rightarrow 2CH_2Br_2$ was 13.05 kcal/mol at DK−CCSD(T)/Aug-VTZ level and 12.92 kcal/mol at DK−CCSD(T)/Aug-VQZ level. [e] From equilibrium study.[49] [f] From two independent calorimetric hydrogenation studies.[50] [g] This radical exhibits very strong nondynamical correlation effects; hence, CCSD(T) will have an error of 1−3 kcal/mol. [h] Overestimated by up to about 0.5 kcal/mol due to basis set incompleteness in carbon (1s) contribution (see text). [i] Calculated at the DK-CCSD(T)/Aug-VTZ level of theory.

thermal corrections (Δhcf_{298}) in the reactions were calculated similarly. These numbers were then combined according to

$$\Delta E_0(\text{react}) = \Delta E_e(\text{react}) + \Delta ZPVE \tag{9}$$

and

$$\Delta_r H_{298} = \Delta E_0(\text{react}) + \Delta hcf_{298} \tag{10}$$

so that enthalpies of formation were finally obtained by the formula

$$\Delta_f H°(C_xH_yBr_z, 298\ K) = \Delta_f H°(C_xH_{y+z}, 298\ K) + z\Delta_f H°(HBr, 298\ K) - z\Delta_f H°(H_2, 298K) - \Delta_r H_{298} \tag{11}$$

The experimental heats of formation of the C_xH_{y+z} species were taken from the compilation by Parthiban and Martin.[13] The value for HBr was taken from the NIST Webbook.[9] $\Delta_f H°$(298 K) of H_2 is zero by definition. The computed heat of formation of CBr includes the spin−orbit corrections of CH and CBr given by Huber and Herzberg.[28]

The concept of isogyric reactions can be taken one step further using isodesmic reactions. Here, not only the number of electron pairs, but also the number of bonds of each formal type (e.g., C−C, C═C, C≡C, C−H, C−Br), are preserved. In this case, errors in correlation energy will largely cancel out for each bond. A "good" (i.e., well-balanced) isodesmic reaction should have a near-zero heat of reaction since similar bonds are broken and formed.[48]

The simplest series of isodesmic reactions that can be applied to our set of brominated species is

$$C_xH_yBr_z + zCH_4 \rightarrow C_xH_{y+z} + zCH_3Br \tag{12}$$

which is, in a way, the isodesmic equivalent of reaction 7. When computing the enthalpy of formation of the brominated compounds using the isodesmic equivalents of eqs 8−11 (i.e., with CH_4 and CH_3Br replacing H_2 and HBr, respectively), the last step requires the enthalpy of formation of CH_3Br. Three experimental values are listed in the NIST Webbook:[9] −8.2 ± 0.2 kcal/mol from an equilibrium study,[49] and two nearly identical values of −9.0 ± 0.32 and −8.97 ± 0.35 kcal/mol from two independent calorimetric hydrogenation studies.[50] Due to this uncertainty, the W2DK value of $\Delta_f H°$(298 K) = −8.71 kcal/mol was used instead. This value is near the average of the three experimental numbers and close to the value of −8.63 kcal/mol calculated using W2 theory[51] and a more recent benchmark calculation of −8.8 kcal/mol.[52]

The isodesmic reactions are better "balanced" than their isogyric analogues, in the sense that their $\Delta_r H_{298}$, $\Delta ZPVE$ and

TABLE 4: Comparison of the DK-CCSD(T)/Aug-VTZ Binding Energies (Used in Isogyric and Isodesmic Reactions) with the W2DK Values (Energies in kcal/mol)

	TAE_e	
compounds	AVTZ[a]	W2DK[b]
CBr	75.36	78.96
CBr_2	135.45	143.10
CBr_4	238.95	251.41
CH_2Br_2	331.26	340.62
CH_3Br	373.20	380.94
C_2Br	212.36	222.03
C_2Br_2	305.76	319.65
C_2HBr	350.12	362.17

	ΔE_e(react)	
reactions	AVTZ[a]	W2DK[b]
$C_2H_2 + C_2Br_2 \rightarrow 2\ C_2HBr$	−0.13	−0.15
$C_2Br_2 + CH_4 \rightarrow 2\ CH_3Br$	−1.32	−1.32
$CBr + OH \rightarrow BrO + CH$	46.07	47.07
$CBr + C_2HBr \rightarrow CH + C_2Br_2$	37.43	38.11

[a] These values are the sum of the AVTZ SCF + CCSD(T) energies and the spin−orbit corrections. [b] These values were calculated as the sum of the Q5 extrapolation of SCF and CCSD(T), TQ extrapolation of 3d correlation, deep-core contribution and spin−orbit splittings. See text for further details.

TABLE 5: Components of the Bottom-of-the-Well Reaction Energies (ΔE_e, kcal/mol) of Isogyric and Isodesmic Reactions

	SCF[a]	CCSD[a]	(T)[a]	3d corr[b]	deep core[c]
		$C_2H_2 + C_2Br_2 \rightarrow 2C_2HBr$			
TZ	−0.94	0.59	0.22	−0.05	−0.01
QZ	−0.90	0.56	0.22	−0.04	
5Z	−0.90	0.56	0.22		
extrap (TQ)	−0.88	0.54	0.23	−0.03	
extrap (Q5)	−0.90	0.56	0.22		
		$CH_2Br_2 + CH_4 \rightarrow 2CH_3Br$			
TZ	−4.95	2.96	0.68	0.04	0.03
QZ	−4.88	2.83	0.71	0.00	
5Z	−4.87	2.82	0.72		
extrap. (TQ)	−4.83	2.75	0.74	−0.02	
extrap. (Q5)	−4.86	2.81	0.73		
		CBr + OH → BrO + CH (Spin−Orbit Correction = −0.46)[d]			
TZ	50.00	−3.93	0.47	0.42	−0.07
QZ	49.71	−3.27	0.45	0.57	
5Z	49.58	−3.12	0.45		
extrap (TQ)	49.52	−2.84	0.44	0.67	
extrap (Q5)	49.45	−2.97	0.45		
		$CBr + C_2HBr \rightarrow CH + C_2Br_2$ (Spin−Orbit Correction = +0.63)[d]			
TZ	29.44	5.47	1.90	0.12	−0.12
QZ	29.38	5.88	1.97	0.14	
5Z	29.34	6.00	2.00		
extrap (TQ)	29.33	6.16	2.01	0.15	
extrap (Q5)	29.29	6.12	2.03		

[a] SCF, CCSD and (T) calculations performed with the AV*n*Z basis sets. [b] 3d contribution to the correlation energy calculated with the ACV*n*Z basis sets. [c] Deep-core contribution to the correlation energy calculated with the CV*n*Z basis sets. [d] Spin−orbit splittings were taken from refs 27 and 28; see text.

Δhcf_{298} are much closer to zero. For example, the average absolute value of $\Delta_r H_{298}$ is about 8 kcal/mol for the isodesmic reactions but over 40 kcal/mol for the isogyric reactions. Hence, the sensitivity of the reaction energy to the level of theory is expected to be weaker, and the isodesmic $\Delta_f H°(298\ K)$ values are, therefore, probably more accurate.

The heats of formation computed via isogyric and isodesmic reactions are listed in Table 3. These two sets of values differ by only about 0.3 kcal/mol on average; the isodesmic results agree with the W2DK calculations to within less than 0.7 kcal/mol in all cases. The sole exception, which will be examined in detail hereinafter, is CBr where a difference of 1.3 kcal/mol is found.

For the sake of comparison to other common methods, G2 calculations[14,15] were also carried out on these systems. Considering the highly approximate character of G2 theory, the agreement with our more rigorous calculations can only be described as remarkable. The main exceptions are the various isomers of C_2HBr_2, where discrepancies are around 2−3 kcal/mol. The G2 calculations for these isomers all suffer from significant "spin contamination", that is, the unrestricted SCF algorithm used by GAUSSIAN 03 generates open-shell solutions that are not exact eigenfunctions of the $\langle S^2 \rangle$ operator, and in this case the "doublet" solutions contain significant contribution from low-lying quartet states. For the other molecules, the discrepancies are more in line with the previously reported[15] mean absolute deviation of 1.37 kcal/mol for a test set of 40 reaction energies involving third-row species. The errors, however, are clearly not systematic. Taken together with the known tendency of G2 to occasionally exhibit very large errors,[13,53,54] they stress the necessity for more rigorous calculations, such as those carried out in the present work.

Some general observations are in order about the W2DK data and their component breakdown (Table 2). Convergence of the SCF, valence CCSD, and valence (T) components is as smooth as one can reasonably expect. The (3d) correlation in bromine is significant at our accuracy level, and its contribution to the total atomization energy increases roughly proportional to the number of bromine atoms, to reach 3.12 kcal/mol at the DK-CCSD(T)/Aug-CVTZ level in CBr_4. This latter number appears to be an upper limit, as the DK-CCSD(T)/Aug-CVQZ values, where available, are systematically smaller than their DK-CCSD(T)/Aug-CVTZ counterparts.

The deep-core contribution appears fairly significant at first sight. However, by comparison with CCSD(T)/CVTZ values[55] for the (1s) core contributions in CH_4 and C_2H_2 (1.05 and 1.90 kcal/mol, respectively), we can attribute essentially all of the deep-core contribution to the carbon (1s) orbitals. Unfortunately, these cannot be correlated separately from the (3s, 3p) orbitals of bromine (which are *higher* in energy), and therefore, calculating its contribution in CBr_4 would require correlating no less than 106 electrons. However, considering how small the deep-core contribution is in CBr (0.03 kcal/mol) and CBr_2 (0.00 kcal/mol), it can be safely assumed to be very small in CBr_4 as well.

(1s) core contributions near the basis set limit are available for CH_4 and C_2H_2 (1.25 and 2.44 kcal/mol, respectively).[56] Considering the strongly additive character of core correlation contributions in hydrocarbons−in fact, it was found that they can be very well approximated as the sum of all CC and CH bond orders multiplied by 0.297(4) kcal/mol[56]—we can prorate the basis set incompleteness error in the C(1s) contributions, finding it to be about 0.10 and 0.15 kcal/mol for CH_2Br_2, and CH_3Br, respectively, and 0.41 and 0.47 kcal/mol, respectively, for C_2Br_2 and C_2HBr. This explains much of the discrepancy between the direct and isodesmic (or isogyric) heats of formation for these species. Note in the top half of Table 5 that the contributions of (3d) correlation and "deep-core" correlation to the corresponding isodesmic reaction energies are exceedingly small.

The Case of CBr and BrO. It can be seen from Table 3 that there is a discrepancy of more than 1.4 kcal/mol between the heats of formation of CBr computed directly using W2DK and via either the isogyric reaction

$$CBr + H_2 \rightarrow CH + HBr \quad (13)$$

or the isodesmic reaction

$$CBr + CH_4 \rightarrow CH + CH_3Br \quad (14)$$

The uncertainty associated with the experimental results is too large to resolve this disagreement.

In an attempt to explain it, we studied a similar system, BrO. The enthalpy of formation of this species, calculated directly (W2DK), is $\Delta_fH°(298\text{ K}) = 30.85$ kcal/mol, reasonably close to the experimental value of 30.16 ± 0.41 kcal/mol.[57] However, using the isogyric reaction

$$BrO + H_2 \rightarrow OH + HBr \quad (15)$$

a value of 31.37 kcal/mol is obtained, 0.52 kcal/mol higher than the direct calculation, and 1.21 kcal/mol higher than the experimental value. It is, therefore, probable that the problem resides with the indirect methods as the radicals on both sides of the equations (CBr vs CH, BrO vs OH) are just too dissimilar.

Another method of computing the heat of formation of CBr is via the reaction

$$CBr + OH \rightarrow CH + BrO \quad (16)$$

This is not isodesmic but may be termed "homodesmic". On each side of the equation, there is one HA($^2\Pi$) and one BrA($^2\Pi$) radical, where A is either carbon or oxygen. In this case, $\Delta_fH°$(298 K) of CBr is calculated to be 118.73 kcal/mol, close to the result of the W2DK calculation. One reason for good error compensation in this reaction—despite its fairly strong endothermicity (Tables 4 and 5)—is that CH and OH on one hand, and CBr and BrO on the other hand, exhibit similar nondynamical correlation effects.

Properties of Individual Species. The molecular parameters, specifically the moments of inertia and the harmonic vibrations, were calculated for all the species reported at the B97-1/Aug-VTZ level of theory. A limited number of calculations were also done using B3LYP/6-31G(d,p), and C_2Br_4 and C_2Br_6 were also examined at the B3LYP/6-31G(d) level.

$CHBr_3$ (Bromoform). Its thermodynamic functions were calculated by Kudchadker and Kudchadker in 1974;[58] their recommended value for the enthalpy of formation was taken from an old NBS circular to be 4.0 kcal/mol. Newer experimental enthalpies of formation and an IR spectrum are given in the NIST 2000 Webbook.[9] The enthalpy of formation seems to be in dispute between Papina et al.[59] (13.24 ± 0.79 kcal/mol) and Bickerton et al.[36] (5.7 ± 1.1 kcal/mol). The Webbook prefers Papina's value, and our own isodesmic value, 12.97 kcal/mol, is in close agreement with it. Paddison and Tschuikow-Roux obtained from MP4/6-31G**//MP2/6-31G* isodesmic reaction energies a value of 12.16 ± 0.7 kcal/mol.[44] The B97-1/Aug-cc-pVTZ frequencies, which agree well with the experimental data,[9] have been used in constructing the thermodynamic functions (see Supporting Information, Table 8).

$CHBr_2$ (Dibromomethyl Radical). The enthalpy of formation of this radical is estimated by Kerr[34] to be 44.98 ± 2.2 kcal/mol. The Thergas[39] estimated value is higher: 48.34 kcal/mol. Paddison and Tschuikow-Roux[44] report a value of 48.11 ± 0.6 kcal/mol from MP4/6-31G**//MP2/6-31G* isodesmic reaction energies, while Lazarou et al.[42] obtained 47.06 kcal/mol using CCSD(T) basis set extrapolations. Our isodesmic calculated value is close to a group equivalent estimate of 47.44 kcal/mol.[36] The molecular parameters were calculated at the B97-1/Aug-cc-pVTZ level; the Jacox[9] compilation contains experimental frequencies for three bands, which agree well with our calculations (Table 9 in the Supporting Information).

CHBr (Bromomethylydene). The only experimental value found was a mass spectrometric measurement of 89.1 ± 4.3 kcal/mol by Nibbering and co-workers.[33] A previous benchmark calculation by Dixon et al.[47] found 90.5 ± 0.7 kcal/mol, in excellent agreement with our isodesmic DK-CCSD(T)/Aug-VTZ value of 90.31 kcal/mol. An earlier estimate, based on semiempirical calculations, was 81.26 ± 5 kcal/mol.[40] Lazarou et al.[42] obtained 91.23 kcal/mol from CCSD(T) basis set extrapolations. The molecular properties (Table 10 in the Supporting Information) were calculated at the B97-1/Aug-cc-pVTZ level of theory. Vibrational frequencies agree well with the CCSD(T)/aug-cc-pVTZ values of Dixon et al.,[47] but less so (expectedly) with an earlier HF/STO-3G* calculation.[60]

CBr_4 (Carbon Tetrabromide). Thermodynamic functions of CBr_4 were calculated by Kudchadker and Kudchadker,[58] based on an enthalpy of formation of 19 kcal/mol, which they took from an 1968 NBS circular. This compound is listed in the JANAF[7] and TRC[31] tables with an estimated enthalpy of formation of 12 kcal/mol. Binkerton[36] lists 20.05 kcal/mol while Gurvich[29] recommends 28.68 kcal/mol based on King, Golden, and Benson.[61] Paddison and Tschuikow-Roux[44] obtained 25.23 ± 0.8 kcal/mol from MP4/6-31G**//MP2/6-31G* isodesmic reaction energies. Our W2DK calculation yields $\Delta_fH_{298} = 28.49$ ±1.5 kcal/mol, very close to Gurvich's analysis. (See Table 11 in the Supporting Information.)

CBr_3 (Tribromomethyl Radical). The enthalpy of formation of CBr_3 is listed by Kerr[34] as 49.5 ± 1.9 kcal/mol. It was also listed by Gurvich[29] as 56.17 kcal/mol, and Dieter and Nieman[10] reported 64.7 kcal/mol. For this species, Paddison and Tschuikow-Roux[44] obtained a value of 55.36 ± 0.7 kcal/mol, very close to our CCSD(T)/Aug-VTZ isodesmic value of 55.50 kcal/mol. Molecular parameters were obtained at the B97-1/Aug-VTZ level (see Table 12 in the Supporting Information).

CBr_2 (Dibromomethylene). The enthalpy of formation is reported by Dittmer and Nieman[10] (84.3 kcal/mol) and by Gurvich[29] (80.45 kcal/mol). Theoretical calculations include 80.5 ± 2 kcal/mol by Sendt and Bacskay,[43] and 85.35 kcal/mol from small-basis set extrapolations by Lazarou et al.[42] Our W2DK calculation of 82.10 kcal/mol falls midway between Gurvich and Lazarou on one end and Ditter and Nieman on the other. The disagreement with the earlier benchmark calculation of Dixon et al., 83.7 ± 0.7 kcal/mol,[47] primarily results from the inner-shell correlation contributions, which add up to 1.35 kcal/mol in the present work but 0.00 kcal/mol in Dixon et al.[47] We note that they used a CVTZ-type basis set for both (3d) and deep core contributions, while we used Aug-CVTZ and Aug-CVQZ basis sets for the (3d) contribution and extrapolated it to the infinite basis limit. Jacox[9] lists experimental vibrations very close to the CCSD(T)/aug-cc-pVTZ data of Dixon et al. as well as our B97-1/Aug-VTZ calculations, which were used in computing the thermodynamic functions. The moments of inertia were likewise derived from the B97-1/Aug-VTZ geometry (Table 13 in the Supporting Information).

CBr (Bromomethylidene). This compound was calculated in the JANAF Tables[7] with $\Delta_fH_{298} = 122 \pm 15.1$ kcal/mol and by Gurvich[29] with $\Delta_fH_{298} = 117.22 \pm 8.4$ kcal/mol. Lazarou et al. calculated, by CCSD(T) basis set extrapolations, a value of 119.55 kcal/mol.[42] Our W2DK calculations fall between the Gurvich[29] and JANAF[7] values ($\Delta_fH_{298} = 118.51$ kcal/mol). The isodesmic value discussed above, 119.08 kcal/mol, is in excellent agreement with the benchmark ab initio calculation of Dixon et al.[47] The molecular parameters once more agree well between their CCSD(T)/aug-cc-pV5Z data, experiment, and our B97-1/Aug-VTZ calculation (see Table 14 in the Supporting Information).

C_2HBr (Bromoacetylene). The enthalpy of formation of this compound was measured by Okabe[62] and this value of 64.3 ± 1.5 kcal/mol proposed by the NIST Webbook[9] is much higher than the estimates of ~50.5 kcal/mol made by Benson[11,39] and Yoneda.[39] Our W2DK value is even higher, at 67.50 kcal/mol, which is probably too high by about 0.5 kcal/mol in view of the underestimated carbon(1s) core correlation contribution (see above). Taking this into account will yield a value close to the isodesmic result of 66.91 kcal/mol (see above). Shimanouchi[9] lists the vibrational assignment of this species and we compared it to our B97-1/Aug-VTZ calculation (see Table 15 in the Supporting Information). There are some minor differences. A measurement by Vaittinen et al.[63] presents only three of the compound's vibrations, in favor of Shimanouchi's assignment.

C_2HBr_2 (*trans*-Dibromovinyl Radical). Our isodesmically derived enthalpy of formation is 79.73 kcal/mol. In this case, the Thergas[39] estimate comes within 1 kcal/mol of our calculation. The molecular parameters were calculated at both at the B97-1/Aug-VTZ and B3LYP/6-31G(d,p) levels, frequencies in the latter case being scaled by 0.955[64] (see Table 16 in the Supporting Information).

C_2HBr_3 (Tribromoethylene). There are no experimental data for the enthalpy of formation of this compound. The estimates of Thergas[39] and NIST 94[72] are similar: ~20 and 14 kcal/mol, respectively, both much lower than our CCSD(T)/Aug-VTZ isodesmic reaction method calculation of 34.46 kcal/mol. The molecular properties were calculated using B97-1/Aug-VTZ. Additionally B3LYP/6-31G(d,p) calculations were performed. The frequencies obtained at the latter level were scaled by 0.955.[64] The vibrations are compared with IR values[9] (see Table 17 in the Supporting Information).

C_2HBr_4 (1,1,2,2- and 1,1,1,2-Tetrabromoethyl Radicals). To our knowledge, no experimental data are available for these radicals. The heat of formation of the first compound was very crudely estimated to be 32.88 ± 6 kcal/mol by Burcat.[40] Our DK-CCSD(T)/Aug-VTZ isodesmic calculations yield 52.30 and 58.23 kcal/mol, respectively, for the two species. Moments of inertia and vibrational frequencies were again calculated at the same two levels of theory as the previous entry (see Tables 18 and 19 in the Supporting Information).

C_2HBr_5 (Pentabromoethane). No data are available for this compound. The Thergas[39] enthalpy of formation was estimated as −11.62 kcal/mol with the Yoneda method and 9.9 kcal/mol using Benson's method, both very far from the DK-CCSD(T)/Aug-VTZ isodesmic calculated value of 27.03 kcal/mol, which is the best available result. As before, the molecular parameters were calculated at both B97-1/Aug-VTZ and B3LYP/6-31G-(d) levels of theory, and frequencies of the latter were scaled by 0.955.[64] The reduced moment of inertia around the C−C bond was calculated using Wang's program.[70] The rotational barrier was calculated by Ruscic and Burcat[68] (see Table 20 in the Supporting Information).

C_2Br (Bromoethyne Radical). The enthalpy of formation of this radical was calculated as 149.09 kcal/mol at the W2DK level. For comparison, the NIST 1994[72] estimate was 126.6 kcal/mol. The molecular properties were calculated at B97-1/Aug-VTZ level (see Table 21 in the Supporting Information). Because of low-lying excited states, this radical both exhibits severe nondynamical correlation effects and appears to undergo a pseudo-Renner−Teller distortion. We optimized the geometry by means of a variety of ab initio and DFT methods and consistently obtained bent geometries and a single imaginary frequency at the linear geometry. A benchmark ab initio study using multireference methods, and perhaps accounting for vibronic coupling, would be highly desirable.

C_2Br_2 (Dibromoacetylene). Dewar and Healy[65] using the obsolete semiempirical MNDO method report an enthalpy of formation of 61.8 kcal/mol for this linear molecule. Our direct W2DK heat of formation was calculated as 80.14 kcal/mol, which is probably too high by about 0.5 kcal/mol in view of the underestimated carbon(1s) core correlation contribution (see above). Taking this into account will yield a value close to the isodesmic result of 79.73 kcal/mol (see above). The spectrum of this molecule was assigned by Shimanouchi.[9] A new DFT calculation by Yoshida et al.[66] is also given for comparison. Our molecular parameters were calculated at the B97-1/Aug-VTZ level (see Table 22 in the Supporting Information).

C_2Br_3 (Tribromovinyl Radical). No data were found in the literature for this radical. The Thergas[39] enthalpy of formation estimate is 75.61 kcal/mol, much lower than our DK-CCSD-(T)/Aug-VTZ isodesmic result of 92.11 kcal/mol. The molecular properties were calculated at the B97-1/Aug-VTZ level (see Table 23 in the Supporting Information).

C_2Br_4 Tetrabromoethylene. Once again, no experimental heat of formation could be found in the literature for this compound. Our isodesmic DK-CCSD(T)/Aug-VTZ value is 45.43 kcal/mol, grossly at variance with estimates using group additivity methods (~14.4 kcal/mol).[38,59] The molecular parameters were calculated at the B97-1/aug-VTZ and B3LYP/6-31G(d) levels of theory. The spectral assignment of Shimanouchi[9] was adopted although there are small differences from the experimental IR values[9] (see Table 24 in the Supporting Information).

C_2Br_5 (Pentabromoethyl Radical). This compound is not referred in the literature and no approximation can be made using Benson's method.[39] Our calculation for the enthalpy of formation was performed using the CCSD(T)/Aug-VTZ isodesmic reaction method, and we obtained 67.70 kcal/mol. The molecular constants were taken from B97-1/Aug-VTZ calculations, and the internal reduced moment of rotation was calculated using Wang's program.[70] The internal rotational barrier was approximated to be equal to that[68] of C_2Br_6 (see Table 25 in the Supporting Information).

C_2Br_6 (Hexabromoethane). Kudchadker and Kudchadker[67] estimated the heat of formation of hexabromoethane to be 39.17 kcal/mol, which is surprisingly close to our isodesmic DK-CCSD(T)/Aug-VTZ result of 39.55 kcal/mol. The B97-1/Aug-VTZ calculations for the molecular parameters are compared with the results of B3LYP/6-31G(d), which were also the source for the internal rotational barrier calculated by Ruscic and Burcat[68] (see Table 26 in the Supporting Information).

Thermodynamic Functions. The ideal gas thermodynamic calculations of all the species described above were performed using the McBride and Gordon[69] PAC99 thermodynamic program in the temperature range of 50 to 6000 K. The rigid rotor harmonic oscillator approximation (RRHO) was used as is customary for all polyatomic species. The bimolecular species CBr was treated by the JANAF method for diatomic species included in PAC99. The input for this program includes the following: molecular vibrations, moments of inertia, the enthalpy of formation at 298 K, the symmetry of the molecule, and its statistical weight. Where needed, the calculated fundamental frequencies were supplemented with internal rotation information calculated using the Cartesian coordinates and Wang's program.[70] The results of the thermodynamic calcula-

TABLE 6: Calculated Thermodynamic Properties of the Compounds in This Research (cal/mol·K)

species	$\Delta_f H_{298}$, kcal/mol	S_{298}	C_p										
			298	400	500	600	800	1000	1200	1500	2000	2500	3000
$CHBr_3$	12.97	78.93	16.98	18.81	20.10	21.04	22.30	23.12	23.70	24.29	24.87	25.18	25.37
$CHBr_2$	47.44	71.36	13.10	14.44	15.35	16.00	16.90	17.51	17.97	18.46	18.97	19.25	19.43
CHBr	90.12	60.44	9.51	10.49	11.15	11.58	12.13	12.49	12.76	13.06	13.38	13.59	13.76
CBr_4	28.49	85.61	21.79	23.20	24.01	24.51	25.05	25.32	25.47	25.60	25.70	25.75	25.77
CBr_3	55.50	80.60	16.53	17.63	18.29	18.71	19.18	19.41	19.55	19.66	19.75	19.80	19.82
CBr_2	82.10	69.00	11.78	12.53	12.95	13.22	13.50	13.64	13.73	13.83	14.08	14.51	15.03
CBr	118.51	55.18	7.74	8.12	8.36	8.51	8.68	8.77	8.82	8.86	8.90	8.91	8.92
C_2HBr	67.50	60.40	13.17	14.54	15.40	16.04	17.01	17.75	18.34	18.99	19.66	20.04	20.27
C_2HBr_2 trans	79.73	78.08	16.32	18.05	19.34	20.32	21.71	22.66	23.33	24.03	24.70	25.07	25.28
C_2HBr_3	34.46	86.04	20.46	22.79	24.45	25.68	27.35	28.43	29.17	29.92	30.63	31.01	31.23
$CHBr_2CBr_2$	52.30	100.14	25.53	28.02	29.79	31.06	32.79	33.89	34.64	35.33	35.84	35.99	36.20
CBr_3CHBr	58.23	99.65	27.10	29.42	30.93	31.99	33.39	34.31	34.94	35.52	35.95	36.06	36.07
C_2HBr_5	27.03	104.97	30.26	33.17	35.17	36.61	38.48	39.67	40.46	41.20	41.74	41.91	41.95
C_2Br	149.06	70.51	10.78	11.34	11.77	12.13	12.67	13.02	13.25	13.46	13.64	13.74	13.79
C_2Br_2	80.14	70.38	16.27	17.20	17.80	18.26	18.93	19.41	19.75	20.08	20.39	20.55	20.64
C_2Br_3	92.11	88.41	19.90	21.44	22.44	23.15	24.11	24.60	24.93	25.23	25.48	25.60	25.67
C_2Br_4	45.43	92.59	24.43	26.39	27.69	28.60	29.74	30.38	30.77	31.12	31.40	31.54	31.64
C_2Br_5	67.70	106.28	30.15	32.38	33.77	34.64	35.51	35.83	35.94	35.97	35.93	35.89	35.86
C_2Br_6	39.55	109.73	35.05	37.63	39.18	40.16	41.27	41.86	42.22	42.55	42.82	42.89	42.84

tions are presented for all the species in Table 6 in the Benson table format[11] (i.e., heat of formation $\Delta_f H$ and entropy S at 298 K and heat capacity C_p as a function of temperature). The values are taken from the original NASA program calculation. A polynomial form of the results is given in an Internet database.[40] The molecular properties used to calculate the data in Table 6 are presented as electronic Supporting Information.

Accuracy of Calculations. Except for C_2Br, the thermochemical data calculated above can be safely assumed to be accurate to 1 kcal/mol or better. (Extensive benchmarking[12,13,24,51] has shown that W2 theory has mean absolute errors in the 1 kJ/mol range for total atomization energies, with worst-case errors of about 1 kcal/mol unless severe nondynamical correlation is involved.[71] As for the isodesmic reaction energies considered here, Table 5 shows them to be very close to both one-particle basis set saturation and n-particle space convergence at the CCSD(T)/Aug-VTZ level.) To that should be added the uncertainties for the other species involved in the isodesmic reactions.

Although the IR spectra used in our calculations were not fully assigned and analyzed spectroscopically, the calculated frequencies and moments of inertia—where experimental data are available—match the IR spectra and other experimental measurements sufficiently closely that any remaining discrepancy will be less than that inherent in the harmonic oscillator approximation. The variation in the entropies, as great as 2 cal/mol·K, is caused primarily by using different internal rotations with different barrier heights, rather than differences in the vibrational values due to improper assignment. A comparison of the values obtained in our calculations with the literature or estimation programs[29,39,72] is presented in Table 7.

TABLE 7: Comparison of Estimation Programs or Literature with Our Calculated Entropies and Heat Capacities (cal/mol·K)[a]

bromo species	T, K	Thergas[39]		NIST 94[72]		this study	
		S	C_p	S	C_p	S	C_p
$CHBr_3$	298	78.66	17.07			79.08	16.98
	1000	103.66	23.11			103.742	23.12
$CHBr_2$	298	70.99	13.22			71.364	13.11
	1000					90.175	17.51
CBr	298	*56.03*	*8.49*	**55.80**	**8.61**	55.183	7.74
	1000	*66.68*	*9.00*	**60.32**	**9.05**	65.31	8.77
CBr_2	298	*68.91*	*11.78*			69.000	11.77
	1000	*84.60*	*13.64*			84.69	13.64
CBr_3	298	*79.93*	*16.12*			80.6	16.53
	1000	*101.87*	*19.36*			102.77	19.41
CBr_4	298	*85.55*	*21.73*	**85.58**	**21.79**	85.61	21.79
	1000	*114.59*	*25.31*	**97.57**	**25.32**	114.68	25.32
C_2HBr	298	60.46	13.67	60.8	13.3	60.40	13.17
	1000	79.49	17.80	79.7	17.7	79.32	17.75
C_2HBr_2	298	77.89	15.25			78.08	16.32
	1000	100.99	22.35			101.92	22.66
C_2HBr_3	298	85.80	20.38	85.9	20.4	86.04	20.46
	1000	115.84	28.41	115.8	28.4	116.10	28.43
$CHBr_2CBr_2$	298	98.61	25.91			100.14	22.53
	1000					135.65	33.89
CBr_3CHBr	298	96.71	25.44			99.65	27.10
	1000	133.08	33.24			137.40	34.31
C_2HBr_5	298	91.30	19.48	107.38	29.42	106.56	30.20
	1000	113.55	14.21			149.65	39.41
C_2Br_2	298	70.81	16.58	70.7	16.6	70.37	16.27
	1000	92.75	19.41	92.6	19.4	92.12	19.41
C_2Br_3	298	87.30	19.43			88.41	19.90
	1000	114.19	24.24			115.77	24.60
C_2Br_4	298	92.43	24.56	92.3	24.6	92.59	24.43
	1000	126.26	30.41	126.1	30.4	126.35	30.38
C_2Br_5	298	109.32	29.05			106.28	30.15
	1000					147.18	35.83
C_2Br_6	298	105.64	33.34	105.7	33.4	109.73	35.05
	1000	151.32	40.60		40.6	157.24	41.86

[a] Data in italics are from Gurvich.[29] Data in boldface are from ref 7.

It is widely known that the accepted thermodynamic properties of chlorinated and brominated compounds are of questionable accuracy, and the example of CBr_4 given in the Introduction can be reinforced with that of C_2Cl_6,[30] both being among the most common chemical species. Since all the species presented in this research are calculated with one unified approach, the task of this work was not only to provide a reliable self-consistent set of data but also to identify, for those who prefer experimental data, which results are more reliable than others.

It is therefore appropriate to compare our data, the older used data with their chloro counterparts listed in Table 1. Only the stable chlorinated molecules were calculated/estimated in a single publication[30] while the rest were gathered from different sources. It can be stated that for most chlorinated and brominated compounds, the experimental evidence is either missing, like for C_2Br_6, or the data are highly spread with very high error bars, such as for C_2Cl_6.[30]

Conclusions

We have accurately calculated thermodynamic properties for some two dozen brominated C_1 and C_2 species. For part of these molecules, thermodynamic data were hitherto either wholly absent or associated with large uncertainty intervals.

We also introduced an all-relativistic variant of W2 theory, denoted W2DK, in which all steps are carried out using the Douglas−Kroll (no-pair) approximation and specially optimized and contracted basis sets.

The (3d) correlation in bromine has noticeable effects on atomization energies of bromine compounds, while that of deeper (3s,3p) correlation appears to be close to negligible— despite the (3s,3p) orbitals lying above the carbon (1s) orbitals in energy. Fairly large basis sets (of at least *spdfg* quality) are required to reliably recover this contribution.

Our newly obtained data should represent a significant step forward for the estimation of kinetic rates in modeling of atmospheric processes, particularly those involved in the stratospheric depletion of ozone.

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Supporting Information Available: Geometries (Cartesian coordinates) of all species and computed rotational constants and vibrational frequencies used in calculating Table 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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