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Theoretical C−H Bond Dissociation Enthalpies for CH_3Br and CH_2ClBr

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The enthalpies of formation for the closed-shell molecules CH_3Br and CH_2ClBr, and the free radicals CH_2Br and CHClBr were estimated by ab initio molecular orbital computations using hydrogenation and isodesmic reactions as working chemical reactions. Four variants of theoretical approaches (levels) and three extended basis sets were applied in the calculations. The methods included fourth-order Møller−Plesset perturbation theory (level I), coupled-cluster theory (level II), density functional theory (level III), and Gaussian-2 (G2) theory (level IV). The standard enthalpies of formation values obtained at levels I−IV for both the closed-shell and open-shell species agreed within ±1 kcal mol^{-1} irrespective of the working chemical reactions chosen. No basis set effects were observed. These invariances support the reliability of the computed data and are, for the most part, due to the cancellation of the computational errors as a result of the application of the working chemical reactions where the ab initio energies are combined with established experimental enthalpies of formation. The four methods provided enthalpies of formation values for CH_3Br, CH_2ClBr, and CH_2Br in good agreement with experimental values as well; the calculations supplied the first known enthalpy data for the CHClBr radical. The recommended standard enthalpies of formation (at 298.15 K and 1.00 atm) are the unweighted averages of the results obtained at levels I−IV with the different hydrogenation and isodesmic reactions: CH_3Br, -8.9 ± 0.8; CH_2ClBr, -11.5 ± 1.1; CH_2Br, 40.7 ± 1.1; CHClBr, 35.1 ± 1.5 kcal mol^{-1}. The error limits designate the estimated maximal uncertainties. These enthalpies of formation values correspond to bond dissociation enthalpies of $DH°_{298}(BrH_2C-H) = 101.7 \pm 1.4$ kcal mol^{-1} and $DH°_{298}(BrClHC-H) = 98.7 \pm 1.9$ kcal mol^{-1}.

1. Introduction

The atmospheric chemistry of bromine-containing molecules and free radicals has attracted great attention in the past decade because of the role that bromine atoms play in the catalytic destruction of the earth's protecting ozone layer in the stratosphere.[1,2] In recent years, interest has been renewed following the recognition that the tropospheric reactions of Br atoms and BrO_x radicals are significantly more important than they were thought, particularly in the Artic region and marine boundary layers.[3−5]

Bromine is emitted into the atmosphere mostly in the form of CH_3Br both from anthropogenic and from natural sources. Although in much smaller concentration, CH_2ClBr is also a permanent Br constituent of the troposphere.[1,6,7] CH_3Br and CH_2ClBr release bromine atoms and other bromine-containing free radicals into the air through a series of degradation processes that are initiated by the reactions with OH. In the initiation steps CH_2Br and CHClBr radicals are formed, respectively, which undergo further atmospheric reactions. Understanding the chemistry of these brominated molecules and radicals in the atmosphere requires a knowledge of their thermochemical properties. This is underlined by the observation that the kinetic parameters for many of the atmospheric reactions of CH_3Br, CH_2ClBr, CH_2Br, and CHClBr are not well-known or are not available at all. Under these conditions the respective thermochemical quantities can be used for assessing the kinetic behavior of the reactions. Specifically, activation energies can be estimated by the reaction enthalpies for which reliable enthalpies of formation are needed.

The enthalpy of formation for bromomethane has been well-established experimentally. Reported values are -8.9 ± 0.4 (ref 8), -9.1 ± 0.3 (ref 9), and -8.2 ± 0.2 (ref 10), and two recent compilations recommend a value of -8.5 (refs 11 and 12) (all in kcal mol^{-1}). The CH_2Br radical has not been studied experimentally to the same extent. The critical review of McMillen and Golden[13] cites an early reaction kinetics study[14] as the source of data and recommends $\Delta H°_{f,298}(CH_2Br) = 41.5$ kcal mol^{-1}. Later, Holmes and Lossing[15] determined 40.2 ± 2.0 kcal mol^{-1} for this radical by monoenergetic electron impact experiments. The JPL compilation[12] proposes $\Delta H°_{f,298}(CH_2Br) = 40 \pm 2$ kcal mol^{-1}. These experimentally based enthalpies of formation imply $DH°_{298}(BrH_2C-H) = 102 \pm 2$ kcal mol^{-1}.

Despite its great importance in atmospheric chemistry, methyl bromide has until recently been the subject of relatively few high-level theoretical studies. This can be understood from the fact that such a large electronic system as the bromine atom is computationally demanding. There have been only two recent publications on the theoretical C−H bond energy of CH_3Br.[16,17] Kambanis and co-workers[16] determined rate constants for the reactions of Cl atoms with CH_3Br, CH_2Br_2, and $CHBr_3$ from direct kinetic experiments and performed ab initio calculations at the MP2 level of theory to interpret their experimental results.

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They reported a bond dissociation enthalpy value of DH°$_{298}$(BrH$_2$C−H) = 99.6 kcal mol^{-1}, which translates into $\Delta H°_{f,298}$(CH$_2$Br) = 38.8 kcal mol^{-1} enthalpy of formation for the bromomethyl radical. Very recently, Paddison and Tschuikow-Roux[17] have carried out a theoretical study of the bromomethanes and the bromomethyl radicals at the MP4 level to provide a self-consistent set of structural parameters, vibrational frequencies, and thermochemical data. Their calculations predict $\Delta H°_{f,298}$(CH$_2$Br) = 41.63 ± 0.4 kcal mol^{-1}, which implies DH°$_{298}$(BrH$_2$C−H) = 102.5 ± 0.6 kcal mol^{-1}. In an impressive series of theoretical papers[18−22] Glukhovtsev et al. discussed the energetics and mechanisms of the S$_N$2 nucleophilic reactions of halide anions with methyl halides (including CH$_3$Br) with various high-level molecular orbital calculations that included spin−orbit effects. In these articles theoretical data can be found for the total electronic energy, charge distribution, geometry, and C−Br dissociation enthalpy of CH$_3$Br. A high-level ab initio molecular orbital study has been published on the structures and vibrational spectra of CH$_2$Br and CH$_2$Br$^+$ by Li and Francisco[23] at the beginning of this year.

While the experimental enthalpies of formation values for the CH$_2$ClBr molecule reported by different groups agree fairly well with each other, −11.9 kcal mol^{-1} (ref 24), −9 kcal mol^{-1} (ref 25), −10.7 kcal mol^{-1} (ref 26), to the best of our knowledge, no such data are available for the corresponding radical, CHClBr, either from experiment or from theoretical investigations.

It is generally accepted that the best way of calculating theoretical enthalpy data is the use of a thermochemical reaction (a “working chemical reaction”) where computational errors (specifically basis set effects) tend to cancel. The more direct atomization approach usually gives much less accurate results. The choice of an isodesmic reaction, where the number of bonds and bond types are preserved on both sides of the reaction, is the preferred option whenever it can be applied.[27] The isogyric approach uses a working chemical reaction in which the number of electron pairs is left unchanged.[28] The accuracy of the enthalpies of formation obtained theoretically is conditioned by a few factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and very importantly, the choice of the working chemical reaction used in the evaluation. Sana et al.[29,30] have carried out extensive studies on the requirements of accurately estimating theoretical enthalpies of formation for XYH$_n$ species in connection with isogyric and X−Y hydrogenation reactions as working chemical reactions. They concluded that, on average, the enthalpies of formation were underestimated when the isogyric approach was used and therefore recommended bond hydrogenation.

In the present work we report on a series of theoretical investigations aimed at establishing gas-phase enthalpies of formation for CH$_3$Br, CH$_2$Br, CH$_2$ClBr, and CHClBr by various high-level quantum chemical methods. Isodesmic and bond hydrogenation reactions were applied to compute reaction enthalpies from which standard enthalpies of formation were derived. Our objective has been to investigate the effect of the level of correlation treatment, the basis set, and the choice of the isodesmic and hydrogenation reactions on the theoretical results in order to provide reliable enthalpy data for use in practical applications such as modeling atmospheric chemistry. The computed enthalpies of formation values and the corresponding C−H bond dissociation enthalpies are compared and discussed with literature values.

2. Methods

All ab initio calculations were carried out using the GAUSSIAN 94 system of programs.[31] The geometrical parameters were fully optimized using second-order Møller−Plesset perturbation theory[32] (MP2), with all electrons being included in the correlation treatment (FULL) and using the 6-31G(d,p) basis set. Harmonic vibrational frequencies and zero-point vibrational energies (ZPE) were computed at this same level of theory (MP2=FULL/6-31G(d,p)). The optimized geometrical parameters were used in four distinct theoretical computations (levels I−IV) to obtain total electronic energies.

Level I. The procedure applied here corresponds to single-point calculations of the total electronic energy at the MP4 level with a frozen-core (FC) approximation and single, double, triple, and quadruple substitutions (MP4SDTQ) using the fairly large basis set, the 6-311++G(3d,2p) basis set. We chose the sp diffuse functions (+) because they are known to be of importance for molecules where the electrons are relatively far from the nucleus, such as large electronic systems with lone pairs.[33] The procedure of this energy calculation is indicated by the following notation:

(R-U)MP4SDTQ=FC/6-311++G(3d,2p)//(R-U)MP2=FULL/6-31G(d,p)

Level II. At this level we carried out single-point calculations applying the single and double coupled cluster theory with inclusion of a perturbative estimate for triple excitations,[34] CCSD(T), and using the 6-311++G(3df,2p) basis set. Scuseria and Lee[35] have found an average deviation between the results of the perturbative approximation CCSD(T) and the full CCSDT version of 0.42 kcal mol^{-1} in 14 test calculations. If one excludes the error of 1.89 kcal mol^{-1} they report for the difficult case of CN$^+$, the average difference becomes even smaller, justifying the application of the simpler method. This procedure can be summarized as

CCSD(T)/6-311++G(3df,2p)//(R-U)MP2=FULL/6-31G(d,p)

Level III. In this case, the electronic energies were estimated with density functional theory (DFT). Concretely, exchange and correlation were treated by the B3LYP protocol,[36] which is based on Becke’s three-parameter hybrid method (B3)[37] for combining Hartree−Fock exchange with a local density approximation exchange−correlation functional (LYP).[38,39] Here, we used the 6-311++G(3d2f,3p) basis set. The shorthand notation for this computation is

B3LYP/6-311++G(3d2f,3p)//(R-U)MP2=FULL/6-31G(d,p)

Level IV. The electronic energies at this level of computation were determined by the application of the Gaussian-2 (G2) theory.[40] In brief, it uses structures optimized at the MP2/6-31G(d) level and calculates energies at the MP4/6-311G(d,p) level augmented by corrections for diffuse functions, a correction for higher polarization functions, a correction for correlation effects beyond fourth-order perturbation theory, and an empirical higher-level correction to account for remaining basis set deficiencies. The reliability of the additivity approximations in G2 theory has been verified.[41] These types of calculations are referred to as “G2 theory” in the following discussions.

3. Results and Discussion

3.1. Structure and Vibrational Frequencies. The fully optimized structural parameters, harmonic frequencies, and zero-

TABLE 1: Structural Parameters and Vibrational Frequencies[a]

parameter[b]	CH_3Br[c]	CH_2Br[d]	CH_2BrCl[e]	$CHBrCl$[f]
		Geometry		
R_{CH}	1.082	1.073	1.082	1.077
R_{CBr}	1.944	1.861	1.942	1.869
∠HCBr	107.90	116.63	106.84	115.66
R_{CCl}			1.759	1.700
∠HCCl			109.23	116.60
		Frequency[g]		
	3144	3274	3132	3158
	3144	3123	3037	1219
	3020	1391	1480	854
	1465	930	1237	664
	1465	678	973	516
	1328	403	739	243
	954		658	
	954		601	
	602		233	
		ZPE[g]		
	23.00	14.01	17.28	9.51

[a] Computed at the MP2=FULL/6-31G(d,p) level. [b] Distances are given in angstroms, angles in degrees, frequencies in cm^{-1}, and zero-point energies (ZPE) in kcal mol^{-1}. [c] C_{3v} symmetry was assumed in the calculations. Experimental geometric data: $R_{CH} = 1.095$ Å, $R_{CBr} = 1.939$ Å, ∠HCBr = 107.2° (ref 26). Experimental frequencies: 3056, 3056, 2935, 1443, 1443, 1306, 955, 955, 611 cm^{-1} (ref 48). [d] Experimental geometric data: $R_{CH} = 1.086$ Å, $R_{CBr} = 1.845$ Å, ∠HCBr = 118° (ref 42). Experimental frequencies: 1356, 953, 693, 368 cm^{-1} (ref 49). [e] Experimental geometric data: $R_{CH} = 1.115$ Å (estimated), $R_{CBr} = 1.928$ Å, $R_{CCl} = 1.755$ Å, ∠HCBr = 109.3° (ref 46). [f] Experimental frequencies: 1196, 866 cm^{-1} (ref 49). [g] Computed at the MP2=FULL/6-31G(d,p) level and subsequently scaled by 0.95.

point energies obtained at the MP2=FULL/6-31G(d,p) level are presented in Table 1.

In the geometry optimization of CH_3Br a constrained C_{3v} symmetry was assumed, while the geometries for CH_2Br, CH_2ClBr, and CHClBr were optimized with no symmetry constraints. Structural parameters for CH_3Br and CH_2Br are available both from experiment[26,42] and theory.[16−18,20,23,43] Our computed bond lengths and bond angles compare favorably with the experimental data (see Table 1) and compare satisfactorily with the results of other ab initio studies. The structural optimizations we performed at the MP2 level returned a nonplanar structure (C_s symmetry) for the CH_2Br radical with a dihedral angle of 156.5°. This C_s symmetry is in accordance with the results of other theoretical studies,[16,17,23] while the experimental spectroscopic results[42,44,45] were interpreted on the basis of a planar structure (C_{2v} symmetry). Very recently, Li and Francisco[23] investigated the issue of planarity of the CH_2Br radical in a detailed theoretical study performed at the MP2, CCSD(T), and B3LYP levels of theory. Their calculations predicted a very nearly planar structure for the CH_2Br radical and essentially no inversion barrier. The apparent discrepancy between experiment and theory can be resolved by observing that the CH_2Br radical probably possesses C_s symmetry, but the two indistinguishable C_s configurations rapidly transform through a small barrier at the planar configuration, which is observed in experimental studies as a dynamically planar structure. We repeated the MP2 geometry optimizations with the assumption of a planar (C_{2v}) structure for CH_2Br and found that the total energy was only 0.12 kcal mol^{-1} higher than the nonplanar conformation. In the present context this implies that there are practically no differences in using either the planar or the nonplanar conformations for the theoretical prediction of the enthalpy of formation of the bromomethyl radical. Only few structural parameters are available from the literature for CH_2ClBr and none for CHClBr. Our computed CH_2ClBr bond lengths and bond angles are supported by the scarce experimental data.[46] Similar to the case of the bromomethyl radical, the calculations predicted C_s structure for the CHClBr radical too. Its deviation from planarity is somewhat larger; the dihedral angle is 147.3° at the MP2/6-31G(d,p) level.

Harmonic vibrational frequencies were computed at the MP2=FULL/6-31G(d,p) level of theory on the basis of optimized geometries at the same level of theory. It is well-known that MP2-calculated frequencies are about 5% too large[47] relative to experimental results because of the anharmonicity of the true molecular frequencies. Therefore, the calculated frequencies for all species were multiplied by 0.95. These scaled frequencies are listed and compared with the experimentally measured values in Table 1. It is seen in Table 1 that our computed frequencies compare reasonably well with the experimentally measured values tabulated in Shimanouchi's[48] and Jacox's[49] compilations for CH_3Br and CH_2Br, respectively. Most of the calculated frequencies for CH_2ClBr and CHClBr are the first reported values in the literature. Given in Table 1 are also the theoretical zero-point energies (ZPE).

3.2. Derivation of the Enthalpies of Formation. The standard enthalpies of formation for CH_3Br, CH_2ClBr, CH_2Br, and CHClBr were estimated at each of levels I−IV from a consideration of applicable working chemical reactions where only the enthalpy of formation in question was unknown. The derivations were made according to the following steps: (i) the total electronic energies for the reactants and the products were calculated; (ii) these were corrected for zero-point energies to obtain a theoretical reaction enthalpy at 0 K; (iii) this theoretical reaction enthalpy was combined with the known enthalpies of formation in the reaction to solve for $\Delta H°_{f,0}$, the required enthalpy of formation at 0 K; (iv) a heat correction was applied to get $\Delta H°_{f,298}$.

The following hydrogenation and isodesmic reactions were used as working chemical reactions in the study:

$$CH_3Br + H_2 \rightarrow CH_4 + HBr \tag{R1}$$

$$CH_2Br + H_2 \rightarrow CH_3 + HBr \tag{R2}$$

$$CH_2Br + CH_4 \rightarrow CH_3Br + CH_3 \tag{R3}$$

$$CH_2ClBr + H_2 \rightarrow CH_3Br + HCl \tag{R4}$$

$$CH_2ClBr + H_2 \rightarrow CH_3Cl + HBr \tag{R5}$$

$$CHClBr + H_2 \rightarrow CH_2Br + HCl \tag{R6}$$

$$CHClBr + H_2 \rightarrow CH_2Cl + HBr \tag{R7}$$

$$CHClBr + CH_4 \rightarrow CH_2ClBr + CH_3 \tag{R8}$$

The reference reactants and products in reactions R1−R8 are in most cases H_2, HBr, HCl, CH_3, CH_4, and CH_3Cl, the thermochemical properties of which are very well established. Their $\Delta H°_{f,298}$ values have been taken from the JANAF tables[50] and are summarized in Table 2 together with the other data that were utilized in the calculations of the standard enthalpies of formation for the model species. The total electronic energies obtained at levels I−IV were corrected by the scaled MP2 zero-point energies (see Table 2). The heat corrections were calculated with standard methods of statistical thermodynamics.

TABLE 2: Total Electronic Energies (E_e), Zero-Point Energies (ZPE), Thermal Corrections (TC(298K)), and Standard Enthalpies of Formation ($\Delta H°_{f,298}$) Utilized in the Calculations of the Enthalpies of Formation for CH_3Br, CH_2Br, CH_2ClBr, and $CHClBr$[a]

species	ZPE[b]	TC(298 K)[b]	$\Delta H°_{f,298}$[c]	E_e level I	E_e level II	E_e level III	E_e level IV[d]
H_2	6.27	2.07	0.00	−1.170 23	−1.170 82	−1.179 98	−1.163 05
CH_3	18.33	2.57	34.82	−39.746 10	−39.757 19	−39.857 61	−39.740 83
CH_4	27.78	2.39	−17.89	−40.420 29	−40.432 91	−40.536 55	−40.407 07
HBr	3.76	2.07	−8.70	−2573.124 75	−2573.159 12	−2574.755 68	−2573.169 89
CH_3Br	23.00	1.92	?	−2612.342 66	−2612.390 73	−2614.079 33	−2612.386 38
CH_2Br	14.01	2.65	?	−2611.673 49	−2611.721 47	−2613.408 18	−2611.726 05
HCl	4.24	2.08	−22.06	−460.292 42			−460.336 86
CH_3Cl	23.43	2.46	−20.0	−499.505 70			−499.549 85
CH_2ClBr	17.28	2.93	?	−3071.427 91			−3071.529 65
CH_2Cl	14.29	2.66	29[e]	−498.838 69			−498.891 50
CHClBr	9.51	2.90	?	−3070.765 14			−3070.875 88

[a] Total electronic energies are given in hartrees. Zero-point energies, thermal corrections, and enthalpies of formation are given in kcal mol^{-1}. [b] Calculated in this work at the MP2=FULL/6-31G(d,p) level of theory with 0.95 scaling of the vibrational frequencies. [c] Taken from ref 50. [d] The values given are the G2 enthalpies at 298 K; i.e., they include ZPE + TC. [e] Taken from ref 12.

TABLE 3: Computed Standard Enthalpies of Formation (at 298.15 K and 1.00 atm) for CH_3Br and CH_2Br[a]

level	$\Delta H°_{f,298}(CH_3Br)$ (R1)[b]	$\Delta H°_{f,298}(CH_2Br)$ (R2)[b]	(R3)[b]
I[c]	−8.5	41.7	41.7
II[d]	−9.6	39.8	40.9
III[e]	−8.0	40.5	40.0
IV[f]	−9.3	40.0	40.8

[a] Values are given in kcal mol^{-1}. [b] Number of the working chemical reaction. [c] (R-U)MP4SDTQ=FC/6-311++G(3d,2p)//(R-U)MP2=FULL/6-31G(d,p). [d] CCSD(T)/6311++G(3df,2p)//(RU)MP2=FULL/631G(d,p). [e] B3LYP/6311++G(3d2f,3p)//(R−U)MP2=FULL/6-31G(d,p). [f] G2 theory.

Calculation of $\Delta H°_{f,298}(CH_3Br)$. The standard enthalpy of formation for CH_3Br is accurately known from experiments.[8−12] Therefore, we applied this molecule as a test case for assessing the performance of the different electron correlation methods and basis sets in our calculations. The observations made with CH_3Br are believed to be transferable also to the subsequent studies of CH_2Br, CH_2ClBr, and CHClBr.

The hydrogenation of methyl bromide to methane (reaction (R1)) was used as a working chemical reaction to obtain $\Delta H°_{f,298}(CH_3Br)$. The results of the theoretical computations at levels I−IV are summarized in Table 3. The standard enthalpies of formation obtained differ only slightly, and there is no reason to give preference over either of them. The average of the four determinations is $\Delta H°_{f,298}(CH_3Br) = -8.9 \pm 0.6$ kcal mol^{-1}, where the error given designates one standard deviation. This theoretical enthalpy of formation agrees very well with the average of experimentally reported[8−12] values, i.e., $\Delta H°_{f,298}(CH_3Br) = -8.7 \pm 0.4$ kcal mol^{-1}.

We performed three series of trial computations on CH_3Br to test further for the accuracy of the combinations of the theoretical methods and basis sets used in this work.

(i) To examine the quality of the results obtained with single-reference electron correlation methods, Lee and Taylor[51] proposed the T_1 diagnostics: $T_1 = ||t_1||/N_{elec}^{1/2}$, where $||t_1||$ is the Euclidean norm of the coupled-cluster with single and double excitation amplitudes, and N_{elec} is the number of active electrons in the correlation procedure. It has been suggested[51−52] that a large T_1 value (i.e. $T_1 > 0.02$) is an indication that nondynamical electron correlation effects are important, and therefore, a multireference electron correlation treatment would be more suitable. In the present case, we obtained $T_1 = 0.009$ for CH_3Br and $T_1 = 0.018$ for CH_2Br, values that indicate dynamical correlation behavior for these electronic systems. Thus, the use of single-reference electron correlation methods seems to be justified.

(ii) For frozen-core vs full correlation tests, in a previous paper,[53] which dealt with the theoretical enthalpies of formation for NH_x ($x = 1, 2, 3$), we noted the importance of the core correlation effects. It was determined that the difference in the number of interacting electron pairs between the products and the reactants is the key element to the choice of a working chemical reaction if correlated wave functions are used; the core correlation effects are less important when this difference is small for the reaction. This can be understood, since there has always been some residual correlation error[54] in any basis set expansions of finite size for each pair of electrons. Thus, the hydrogenation reactions are less sensitive to the core correlation effects than their isogyric counterparts because the net number of the interacting electron pairs is smaller. We investigated the effect of electron correlation on the computed CH_3Br enthalpy of formation at the MP4 level of theory by using the R1 hydrogenation reaction and an appropriate isogyric process. The results obtained with the frozen core approach and the full electron correlation are compared in Table 4. The computed enthalpies of formation values are seen to be essentially equal with and without the inclusion of core correlation in the case of the hydrogenation reaction. This may be taken as an indication for the reliability of the level I results obtained in the current study. On the other hand, the application of the isogyric reaction, where the number of the interacting electron pairs are about 2 times larger, provides a substantially higher enthalpy value in the FC approach.

(iii) It is known that the unrestricted MP perturbation theory calculations converge slowly for certain electronic systems.[55,56] In this regard, to estimate the importance of the post-MP4 energy, we employed the fourth-order invariant quantity of Feenberg.[57,58] The resulting correction on the calculated enthalpy of formation was found to be negligible.

In summary, the above trials indicate that the CH_3Br molecule is well described at the theoretical levels used in this work.

Calculation of $\Delta H°_{f,298}(CH_2Br)$. The hydrogenation reaction R2 and the isodesmic reaction R3 were used as working chemical reactions. In the latter case, CH_3Br is one of the reference compounds. Its standard enthalpy of formation was taken from ref 12, i.e., $\Delta H°_{f,298}(CH_3Br) = -8.5$ kcal mol^{-1}. The standard enthalpies of formation determined theoretically for the bromomethyl radical in the current work are listed in Table 3. The average of the eight values obtained at levels I−IV

TABLE 4: Effect of Electron Correlation on the Calculated Enthalpy of Formation for CH_3Br[a]

approach	reaction					diff[b]	$\Delta H^\circ_{f,298}(CH_3Br)$[c]
	CH_3Br +	H2 →	CH_4 +	BrH (hydrogenation)			
FC[d]	(14 × 13/2)[e]	(1)	(8 × 7/2)	(8 × 7/2)		36	−8.5[f]
FULL[g]	(44 × 43/2)	(1)	(10 × 9/2)	(36 × 35/2)		271	−8.6
	CH_3Br +	H →	C +	Br +	2H2 (isogyric)		
FC[d]	(14 × 13/2)		(4 × 3/2)	(7 × 6/2)	2 × (1)	62	−5.6
FULL[g]	(44 × 43/2)		(6 × 5/2)	(35 × 34/2)	2 × (1)	334	−8.0

[a] MP4/6-311++G(3d,2p)//MP2/6-31G(d,p) calculations. [b] The difference in the number of interacting electron pairs between the reactants and the products. [c] The standard enthalpy of formation for CH_3Br is given in kcal mol^{-1}. [d] Frozen core approach. [e] In parentheses the number of the interacting electron pairs is given. [f] Identical with the level I result in Table 3. [g] All electrons are included in the correlation treatment.

TABLE 5: Computed Standard Enthalpies of Formation (at 298.15 K and 1.00 atm) for CH_2ClBr and $CHClBr$[a]

	$\Delta H^\circ_{f,298}(CH_2ClBr)$		$\Delta H^\circ_{f,298}(CHClBr)$		
level	(R4)[b]	(R5)[b]	(R6)[b]	(R7)[b]	(R8)[b]
I[c]	−10.6	−11.6	35.6	35.9	36.6
IV[d]	−11.9	−11.7	33.7	34.4	34.5

[a] Values are given in kcal mol^{-1}. [b] Number of the working chemical reaction. [c] (R-U)MP4SDTQ=FC/6-311++G(3d,2p)//(R-U)MP2=FULL/6-31G(d,p). [d] G2 theory.

TABLE 6: Comparison of the Computed Enthalpies of Formation with Experiment ($T = 298.15$ K, $P = 1.00$ atm)[a]

species	$\Delta H^\circ_{f,298}$/this work[b]	$\Delta H^\circ_{f,298}$/exp[c]	ref
CH_3Br	−8.9 ± 0.8	−8.9	8
		−9.1	9
		−8.2	10
		−8.5	11,12
CH_2Br	40.7 ± 1.1	40 ± 2	12
		41.5	13
		40.2 ± 2	15
CH_2ClBr	−11.5 ± 1.1	−11.9	24
		−9[d]	25
		−10.7	26
CHClBr	35.1 ± 1.5		

[a] The standard enthalpies of formation are given in kcal mol^{-1}. [b] The errors are estimated overall uncertainties (see text). [c] Experimental or critically evaluated data based on experiments; the error limits are those reported by the authors. [d] Estimated by experimental data.

is $\Delta H^\circ_{f,298}(CH_2Br) = 40.7 \pm 0.7$ kcal mol^{-1} ($\pm 1\sigma$). The maximum deviation from this average value is 1 kcal mol^{-1}.

Calculations of $\Delta H^\circ_{f,298}(CH_2ClBr)$ and $\Delta H^\circ_{f,298}(CHClBr)$. In these calculations only the level I and the level IV procedures were applied but in conjunction with five working chemical reactions; reactions R4 and R5 were used for CH_2ClBr, while reactions R6−R8 were used for CHClBr. The computed enthalpies of formation at 298 K are presented in Table 5. Once again, we propose unweighted averaging of the data, which provides results with good precision. These are the following: $\Delta H^\circ_{f,298}(CH_2ClBr) = -11.5 \pm 0.6$ kcal mol^{-1} and $\Delta H^\circ_{f,298}(CHClBr) = 35.1 \pm 1.0$ kcal mol^{-1}, where the error limits quoted are single standard deviations. The maximum deviations are 0.9 and 1.5 kcal mol^{-1} for CH_2ClBr and CHClBr, respectively.

3.3. Discussion of the Enthalpy Results. We set out by pointing out that the combinations of the different theoretical methods and basis sets in levels I−IV and applied in conjunction with the thermochemical reactions R1−R8 have provided enthalpies of formation values in good agreement. This is expressed in an absolute average deviation of 0.6 kcal mol^{-1} from the mean values. The only perceptible trend is observed in connection with the level I results; the enthalpies of formation obtained at this level are slightly but systematically higher on an average by 0.8 kcal mol^{-1}. No significance has been attributed to this disparity; however, as one reaches the 1 kcal mol^{-1} level of accuracy in thermochemical calculations, the sources of error become difficult to pinpoint and the current accuracies of the experimental data allow no firm distinctions to be made either. Therefore, the averages of the different determinations are proposed as final results.

The good agreement between the predicted enthalpies of formation lends credence to them and justifies the averaging. The standard enthalpies of formation for CH_3Br, CH_2ClBr, CH_2Br, and CHClBr recommended from this study are given in Table 6. Attached to them are the estimated maximal uncertainties that were reached from a consideration of the possible sources of errors.

A substantial part of the uncertainties arises from the calculation of the electronic energies. As upper limits, the standard deviations evaluated in the previous section were accepted to account for this uncertainty. The errors, due to zero-point energy corrections, were assessed by choosing the experimental zero-point energies wherever available instead of the theoretical data. The error limits for the enthalpies of formation of the reference species were taken from their literature sources, and a uniformly ±0.3 kcal mol^{-1} error contribution was accepted for the thermal corrections. Standard error propagation methods have been used to calculate the combined uncertainties that appear in Table 6.

In Table 6, along with our theoretical results, we also list experimentally determined enthalpies of formation from the literature for comparison. As was mentioned earlier, there is an excellent agreement between the calculated and experimental[8−12] $\Delta H^\circ_{f,298}$ values for CH_3Br. It is seen in Table 6 that our recommended theoretical enthalpy of formation for the bromomethyl radical agrees most favorably with the experimental result of Holmes and Lossing[15] that was obtained from the measurements of appearance energies for ionic dissociations, but the other reported values[12,13] are also well within the quoted error limits of ±1.1 kcal mol^{-1}. The enthalpy of formation calculated for CH_2ClBr is close to the lower literature values.[24−26] To our knowledge, there are no previously reported enthalpies of formation for the CHClBr radical with which to compare our result. In summary, it can be concluded that the recommended $\Delta H^\circ_{f,298}$ values for CH_3Br, CH_2Br, and CH_2ClBr are in good agreement with experimental results, which may be taken as an indication also for the reliability of the CHClBr enthalpy of formation of 35.1 ± 1.5 kcal mol^{-1} determined in this study the first time.

Very recently, Paddison and Tschuikow-Roux[17] have established a complete thermochemical database for all the bromomethanes and the corresponding bromomethyl radicals by ab initio computations. Their theoretical approach was similar to that applied here at level I; the electron correlation corrections were evaluated at the MP4 level in both studies, but different basis sets were chosen for bromine, as is seen in Table 7 where

TABLE 7: Comparison with the Theoretical Work of Paddison and Tschuikow-Roux for CH_2Br (Ref 17)

computational details	ref 17	this study[a]
geometry	MP2/6-31G(d)	MP2/6-31G(d,p)
total energy	MP4/6-31G(d,p)[b]	MP4/6-311++G(3d,2p)[c]
basis set for Br	SV4P[d]	standard[e]
vibrational frequencies (ZPE)	HF/6-31G(d)[f]	MP2/6-31G(d,p)[g]
working chemical reaction	(R3)	(R2), (R3)
$\Delta H°_{f,298}(CH_2Br)$[h]	41.6	40.7

[a] Corresponds to level I. [b] Single-point calculation at MP2/6-31G(d) optimized geometry. [c] Single-point calculation at MP2/6-31G(d,p) optimized geometry. [d] The polarized split-valence bromine basis set of Andzelm et al. (ref 61). [e] The internal basis set in the GAUSSIAN 94 program suite (ref 31). [f] Scaled by 0.895. [g] Scaled by 0.950. [h] The standard enthalpy of formation for CH_2Br is given in kcal mol^{-1}.

TABLE 8: Level IV (G2 Theory) Calculations of the Enthalpies of Formation by Using the Atomization Reactions[a]

	$\Delta H°_{f,298}$[b]		
species	without s−o[c]	with s−o[d]	selected value[e]
CH_3Br	−11.7	−8.2	−8.9 ± 0.8
CH_2Br	38.3	41.8	40.7 ± 1.1
CH_2ClBr	−13.9	−10.4	−11.5 ± 1.1
CHClBr	32.0	35.5	35.1 ± 1.5

[a] Values are given in kcal mol^{-1}. [b] Standard enthalpies of formation (at 298.15 K and 1.00 atm). [c] Without the inclusion of spin−orbit coupling. [d] With the inclusion of spin−orbit coupling for Br. [e] Recommended by the results of the calculations at levels I−IV applied in conjunction with the working chemical reactions R1−R8 (see text).

we have made a comparison for the CH_2Br radical. Note also that the same working chemical reaction, (reaction R3), was used in the work of Paddison and Tschuikow-Roux and by us. Examination of Table 7 shows agreement between the two calculated $\Delta H°_{f,298}$ values for the bromomethyl radical, revealing essentially no basis set effect.

We have found it of interest to repeat the enthalpy calculations by a consideration of the atomization reactions. That is, the theoretical enthalpies of formation were derived by subtracting the sum of the calculated atomization enthalpies from the known enthalpies of formation of the isolated atoms (taken from ref 50). The results obtained in this way at level IV (G2 theory) are presented in Table 8 along with our recommended enthalpies of formation, which, in turn, were shown to be in good agreement with experimental results. The average absolute deviation between the two sets of data is 2.9 kcal mol^{-1}. Inclusion of spin−orbit effects for Br[59,60] reduces the average absolute deviation to 0.8 kcal mol^{-1}. That is, the G2-theory/atomization reaction approach provides very good estimations for the enthalpies of formation of CH_3Br, CH_2ClBr, CH_2Br, and CHClBr studied. This finding is in line with the conclusions of Curtiss and coauthors[60] who have made a comprehensive assessment of the G2 theory and DFT theories for the computations of enthalpies of formation on a set of 148 molecules referred to as the G2 neutral test set. No bromine-containing species have been included in the G2 test set however. Thus, the present study may be taken as a supplement to the work of Curtiss et al.[60] Our level I and level II computations applied in connection with the atomization reactions performed much less satisfactorily probably because of the substantial residual electron correlation errors. For example, the deviations for CH_3Br are as large as 14.6 and 10.4 kcal mol^{-1}, respectively, at levels I and II. Interestingly, level III (B3LYP//MP2), which is computationally less demanding, does somewhat better, the deviation for CH_3Br being 3.2 kcal mol^{-1}. It is to be recalled, however, that these latter three computational levels all perform very well if they are used with hydrogenation and isodesmic reactions.

From our theoretical enthalpies of formation, which are given in Table 6, we calculated C−H bond dissociation enthalpies ($DH°_{298}$). For this, $\Delta H°_{f,298}(H) = 52.10$ kcal mol^{-1} was taken from ref 50. The recommended standard enthalpies of formation values for CH_3Br, CH_2Br, CH_2ClBr, and CHClBr correspond to the standard C−H bond dissociation enthalpies of $DH°_{298}(BrH_2C{-}H) = 101.7 \pm 1.4$ kcal mol^{-1} and $DH°_{298}(BrHClC{-}H) = 98.7 \pm 1.9$ kcal mol^{-1}. Comparison of these bond dissociation enthalpies with the bond strength in methane, $DH°_{298}(H_3C{-}H) = 104.8 \pm 0.2$ kcal mol^{-1} (ref 50), indicates a gradual weakening of the C−H bond with successive chlorine and bromine substitutions. Such a substitutional effect has long been known to reaction kineticists (see also the discussions in refs 16 and 17), but the present study appears to be the first one to quantify it for CH_3Br and CH_2ClBr by high-level comparative ab initio computations.

Finally, we note that direct reaction kinetics investigations have been underway in our laboratories in cooperation with other groups[62] with the aim of determining more accurate experimental enthalpies of formation for the bromomethyl and chlorobromomethyl free radicals, a task that has been addressed theoretically in the present work.

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