

Structures, Vibrational Frequencies, Thermodynamic Properties, and Bond Dissociation Energies of the Bromomethanes and Bromomethyl Radicals: an Ab Initio Study

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Reported here is a theoretical study of the entire series of bromomethanes ($\text{CH}_{4-n}\text{Br}_n$) and bromomethyl radicals ($\text{CH}_{3-m}\text{Br}_m$) establishing a self-consistent set of structural and thermodynamic information. Ab initio molecular orbital calculations were performed to compute equilibrium geometries for the molecules and radicals initially at the (U)HF/6-31G* and (R)HF/6-31G* levels, respectively, and then refined at the MP2/6-31G* level. Vibrational frequencies were determined for all species at the HF/6-31G* level and comparison with infrared measurements and matrix isolation studies is favorable. Electron correlation contributions were performed by single-point calculations using fourth-order Møller–Plesset perturbation theory for derived MP2/6-31G* geometries. Enthalpies of formation were obtained from a consideration of applicable isodesmic reactions using the derived MP4/6-31G**//MP2/6-31G* total energies in conjunction with experimentally established enthalpies of formation for CH_3Br , CH_4 , and CH_3^\bullet . The calculations predict the following standard enthalpies of formation in kilocalories per mole (at 298 K and 1 atm): CH_2Br_2 , 1.07 ± 0.6 ; CHBr_3 , 12.16 ± 0.7 ; CBr_4 , 25.23 ± 0.8 ; $\text{CH}_2\text{Br}^\bullet$, 41.63 ± 0.4 ; CHBr_2^\bullet , 48.11 ± 0.6 ; and CBr_3^\bullet , 55.36 ± 0.7 . These data are then used to tabulate $\Delta H^\circ_{\text{f,T}}$, $\Delta G^\circ_{\text{f,T}}$, and $K_{\text{f,T}}$ for all species over the temperature range 0–1500 K. Comparison is made to existing thermochemical data through calculation of C–H and C–Br bond dissociation energies.

Introduction

Although bromine is present in the atmosphere in much smaller abundance than chlorine, it nevertheless is extremely important in the destruction of ozone.¹ There are a large number of organic forms of bromine found in the atmosphere, including both natural (CH_3Br , CH_2Br_2 , CHBr_3 , CH_2BrCl , CHBr_2Cl) and anthropogenic (CF_3Br and CF_2BrCl) sources.² Methyl bromide is the most abundant atmospheric source of bromine in the gas phase³ and has received considerable attention recently.^{2,4–6} This has been the result of the estimation of its ozone depletion potential (ODP) being as high as 0.7⁷ and the evidence of a possible significant anthropogenic source.^{2,8} In contrast to CH_3Br , CH_2Br_2 and CHBr_3 are both essentially completely biogenic in origin, being produced by marine macroalgae⁹ and phytoplankton.¹⁰ Recent studies have implicated both the dibromo-^{7,11,12} and tribromo-^{8,13} methanes as important bromine-containing ozone-destroying substances (ODS). The main process whereby CH_3Br and CH_2Br_2 molecules are removed from the atmosphere is through reaction with tropospheric hydroxyl radicals. Bromoform is degraded rapidly through UV photolysis in the troposphere. It is also probable that all three brominated methanes may be destroyed to some degree by Cl atoms in the marine boundary layer.¹⁴

Understanding the chemistry of these brominated methanes in the atmosphere requires a complete thermochemical database of both the molecules ($\text{CH}_{4-n}\text{Br}_n$) and the corresponding radicals ($\text{CH}_{3-m}\text{Br}_m$). Only the thermodynamic properties of CH_3Br are well established; a critical review of the experimental literature may be found in Kudchadker and Kudchadker.¹⁵ Along with a general lack of experimentally measured thermochemical in-

formation on these brominated species, until recently there existed only a few theoretical studies on methyl bromide, and these were at a rather low level of theory.^{16–18} This was undoubtedly due to the computational difficulties in treating ab initio as large an electronic system as bromine. Very recently, however, Kambanis et al.¹⁹ in a study primarily aimed at measuring the absolute rate constants of the reaction of CH_3Br , CH_2Br_2 , and CHBr_3 with Cl atoms, reported theoretical calculations of structural parameters, vibrational frequencies, and bond dissociation enthalpies of several of the bromomethanes and bromomethyl radicals using the GAMESS system of programs.²⁰ Although the trend in their calculated C–H and C–Br bond dissociation energies with increasing bromine substitution is correct, the absolute values do not agree very well with the literature, differing in some cases by more than 7 kcal/mol.

With the importance of the participation of the bromomethanes and bromomethyl radicals in atmospheric chemistry, we present here the results of an ab initio study of all the bromomethyl species using the GAUSSIAN suite of programs.²¹ Complete structural and vibrational frequency data are computed and compared with published results. From a series of related isodesmic reactions with a selected “seed” value for the standard enthalpy of formation of methyl bromide, the standard enthalpies of formation of all the molecules and radicals are evaluated. In addition, standard thermodynamic functions of enthalpy, free energy, entropy, and heat capacity are tabulated as a function of temperature for all species. Bond dissociation enthalpies are computed and discussed with literature values. Preliminary results from this study were published earlier.²²

Method

All ab initio molecular orbital calculations were carried out with the GAUSSIAN 92 system of programs.²¹ Singlet states

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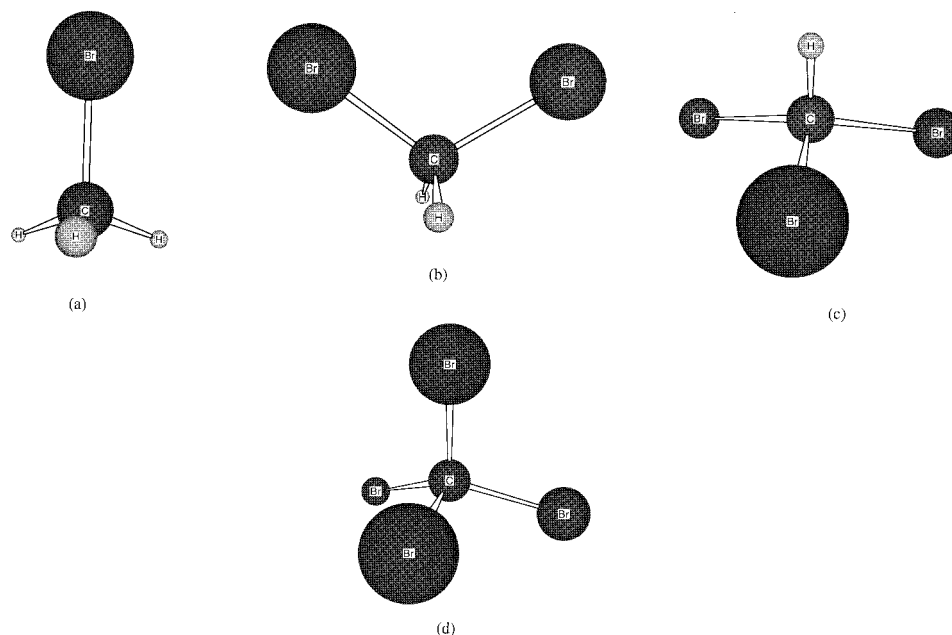


Figure 1. MP2/6-31G* optimized geometries of the bromomethanes: (a) bromomethane; (b) dibromomethane; (c) tribromomethane; and (d) tetrabromomethane.

($\text{CH}_{4-n}\text{Br}_n$ molecules) were calculated by using closed-shell Hartree–Fock theory (RHF)²³ and doublet states ($\text{CH}_{3-m}\text{Br}_m$ radicals) were calculated by using Pople–Nesbet spin unrestricted theory (UHF).²⁴ The internal 6-31G* basis set²⁵ was used for the carbon and hydrogen atoms in both the molecules and the radicals. Since a standard 6-31G* basis set was not available for bromine in the GAUSSIAN 92 molecular orbital packages, the “SV4P” polarized split-valence bromine basis set of Andzelm et al.,²⁶ an alternative originally proposed and tested with favorable results by McGrath and Radom,²⁷ was implemented. The optimized geometries for all species were first determined at the HF/6-31G* level and then refined at the MP2/6-31G* level using analytical methods.²⁸ Total energies for all species were then computed by single-point calculation using fourth-order Møller–Plesset perturbation theory with the 6-31G** basis set (bromine treated with the SV4P basis set). Vibrational frequencies and zero point energies were obtained at the HF/6-31G* level by using analytical second derivatives,²⁹ and the results were then uniformly scaled by 0.8953 to adjust for systematic overestimation of the values at the HF–SCF level.³⁰

Results

I. Geometries: $\text{CH}_{4-n}\text{Br}_n$ Bromomethanes. The fully optimized geometries for all the bromomethanes are presented in Figure 1. The numerical values of the structural parameters including carbon–hydrogen and carbon–bromine bond distances along with applicable bond angles are listed in Table 1. It should be pointed out that the optimizations of all these molecules were performed under assumptions of constrained symmetry; the point groups are to be found in Table 1. Comparison is made to both experimentally determined parameters¹⁵ and those recently computed by Kambanis et al.¹⁹ with the 3-21++G** basis set. Our results compare very favorably with the selected experimental results, with C–H bond distances generally slightly shorter than experimental values and C–Br bond distances a little longer. It is also clear that the 6-31G* basis set has given a significantly better set of structural parameters than the 3-21++G** basis set. The total electronic energies obtained in the geometry optimizations are given in Table 2 along with MP4/6-31G** energies derived from the

TABLE 1: Structural Parameters for Bromomethanes

parameter ^a	experimental ^b	ref 19 ^c	this work ^d
CH_3Br , C_{3v}			
C–H	1.095	1.083	1.087
C–Br	1.939	1.992	1.951
$\angle\text{HCH}$	111.6	111.87	111.1
$\angle\text{HCB}$	107.2	106.95	107.4
CH_2Br_2 , C_{2v}			
C–H	1.097	1.080	1.085
C–Br	1.925	1.969	1.939
$\angle\text{HCH}$	110.9	114.04	112.2
$\angle\text{HCB}$	^e	107.83	107.9
$\angle\text{BrCB}$	112.9	111.55	113.2
CHBr_3 , C_{3v}			
C–H	1.068	1.079	1.075
C–Br	1.930	1.960	1.938
$\angle\text{HCB}$	107.9	107.90	107.4
$\angle\text{BrCB}$	111.0	111.00	111.5
CBr_4 , T_d			
C–Br	1.942	^f	1.946
$\angle\text{BrCB}$	109.5	^f	109.5

^a Units: Bond lengths are given in angstroms; bond angles are given in degrees. ^b Values taken from ref 15. ^c Computed at the MP2/3-21++G** level without any symmetry constraints. ^d Obtained from optimized geometries at the MP2/6-31G* level with constrained symmetry. ^e Not given. ^f Molecule not considered in study.

MP2/6-31G* structures. We note that the MP4/6-31G** energies are uniformly about 0.056 hartree lower than the MP2/6-31G* energies.

$\text{CH}_{3-m}\text{Br}_m$ Bromomethyl Radicals. Figure 2 shows the fully optimized geometries of the bromomethyl radicals at the MP2/6-31G* level. Corresponding structural parameters are given in Table 3. As no experimentally derived bond lengths nor bond angles are reported in the literature for the bromomethyl radicals, comparison is made only to the computed parameters of Kambanis et al.¹⁹ It is of interest to note that the HF/3-21++G** geometries consistently show C–H bond distances that are shorter and C–Br bond distances that are longer than we obtained at the MP2/6-31G* level. This trend was also generally observed in the bromomethanes (see Table 1). The MP2/6-31G**//MP2/6-31G* and MP4/6-31G**//MP2/6-31G*

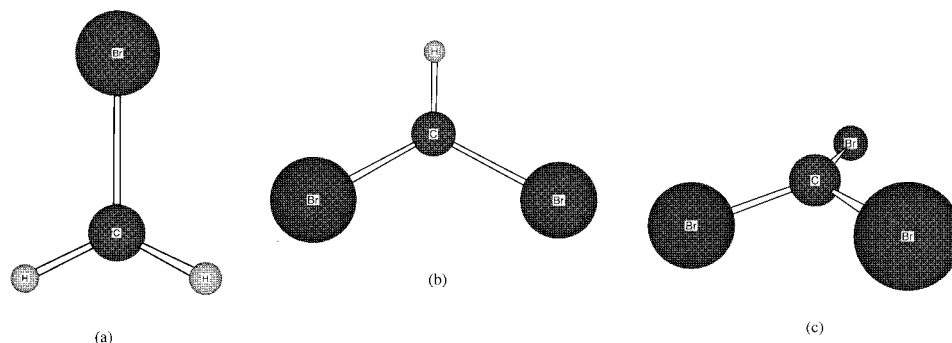


Figure 2. MP2/6-31G* optimized geometries of the bromomethyl radicals: (a) bromomethyl radical; (b) dibromomethyl radical; and (c) tribromomethyl radical.

TABLE 2: Electronic Energies^a and Zero-Point Vibrational Energies (ZPE)^b

species	MP2/6-31G** MP2/6-31G*	MP4/6-31G**// MP2/6-31G*	ZPE (HF/6-31G*)
CH ₄	-40.332 55	-40.388 64	30.0
CH ₃ Br	-2610.008 66	-2610.064 60	25.1
CH ₂ Br ₂	-5179.682 65	-5179.738 38	19.2
CHBr ₃	-7749.353 92	-7749.409 44	12.4
CBr ₄	-10319.021 26	-10319.076 90	5.0
CH ₃ [*]	-39.668 75	-39.714 75	19.4
CH ₂ Br [*]	-2609.348 87	-2609.395 48	15.2
CHBr ₂ [*]	-5179.028 63	-5179.075 45	9.9
CBr ₃ [*]	-7748.706 64	-7748.753 50	3.7

^a Total energies are given in hartrees. ^b Unscaled zero-point vibrational energies (ZPE) are given in kilocalories per mole.

TABLE 3: Structural Parameters for Bromomethyl Radicals

parameter ^a	ref 19 ^b	this work ^c
CH ₂ Br [*] , A' C _s		
C-H	1.069	1.079
C-Br	1.889	1.869
∠HCH	125.40	122.8
∠HCB _r	117.31	116.5
CHBr ₂ [*] , A' C _s		
C-H	1.070	1.082
C-Br	1.883	1.870
∠HCB _r	117.36	115.8
∠BrCB _r	119.32	119.3
CBr ₃ [*] , C _{3v}		
C-Br	1.884	1.880
∠BrCB _r	118.10	116.8

^a Units: Bond lengths are given in angstroms; bond angles are given in degrees. ^b Computed at the HF/3-21++G** level without any symmetry constraints. ^c Obtained from optimized geometries at the MP2/6-31G* level with constrained symmetry for the CBr₃^{*} radical only.

total electronic energies are tabulated in Table 2. The expectation value of S^2 for CH₂Br^{*}, CHBr₂^{*}, and CBr₃^{*} was 0.767, 0.770, and 0.773, respectively, indicating increasing spin contamination with bromine substitution. Similar to the molecules, the radicals show a uniform difference in energies between the two levels of calculation: the MP4/6-31G** values are approximately 0.046 hartree lower. The consistent differences between MP4 and MP2 energies in both the molecules and radicals infers little distinction in derived enthalpies at either levels of theory, the truth of which was borne out in calculation.

II. Vibrational Frequencies. Harmonic vibrational frequencies were calculated for all species at the HF/6-31G* level of theory on the basis of optimized geometries at the same level of theory. As indicated earlier, the frequencies were subse-

TABLE 4: Vibrational Frequencies^a and Moments of Inertia of the Bromomethanes

moments of inertia ^b	observed ^c	ref 19 ^d	this work ^e	IR intensity ^f
CH ₃ Br				
0.057 99	3056 (3055) ^g	3314.5, 3296.9	3040, E	4.1
0.883 91	2935	3173.1	2938, A ₁	28.1
0.883 91	1443 (1447)	1484.3, 1483.1	1449, E	4.4
	1306 (1300)	1359.4	1325, A ₁	56.4
	955 (952)	973.5, 972.7	950, E	5.8
	611 (603)	586.1	573, A ₁	26.4
CH ₂ Br ₂				
0.318 10	3073 (3073)	3344.0	3089, B ₁	1.0
6.867 97	3009 (3006)	3234.1	3004, A ₁	4.3
7.133 18	1382 (1400)	1428.1	1423, A ₁	1.7
	1195 (1194)	1251.0	1219, A ₁	124.8
	1095 (1097)	1149.5	1105, A ₂	0.0
	812 (811)	805.1	809, B ₁	5.5
	653 (649)	630.5	640, B ₂	102.5
	588 (583)	569.4	558, A ₁	7.6
	169	168.0	165, A ₁	0.1
CHBr ₃				
6.7896	3042 (3063)	3329.1	3070, B ₁	3.0
6.7896	1149 (1153)	1202.0, 1201.1	1170, E	56.0
13.3706	669 (667)	658.3, 655.8	667, E	91.3
	541 (542)	519.2	517, A ₁	1.5
	222	215.6	216, A ₁	0.02
	155	151.7, 151.2	149, E	0.03
CBr ₄				
13.1222	672 (675)	<i>h</i>	689, T ₂	80.0
13.1222	267		260, A ₁	0.0
13.1222	182		179, T ₂	0.0
	122		124, E	0.0

^a Units: cm⁻¹. ^b I_a, I_b, I_c; units are 10⁻³⁸ g cm². ^c Taken from ref 32. ^d Calculated at the MP2/3-21++G** level without any symmetry constraints and subsequently scaled by 0.89. ^e Calculated at the HF/6-31G* level and subsequently scaled by 0.8953. ^f Intensity is calculated by the atomic polar method as implemented in GAUSSIAN 92, in kilometers per mole. ^g Matrix isolation IR spectroscopic measurement from refs 33 and 34. ^h Molecule not considered in study.

quently scaled by 0.8953.³⁰ The choice of 0.8953 as an appropriate vibrational frequency scaling factor for HF/6-31G* theoretical frequencies has been further justified by a recent exhaustive study involving 122 molecules by Scott and Radom.³¹ Zero-point vibrational energies (ZPE) were computed for all species from the unscaled theoretically generated frequencies and are listed in Table 2.

Bromomethanes. The vibrational frequencies, IR intensities, and moments of inertia for the four bromomethanes are given in Table 4. Our computed frequencies are compared with both the experimentally measured values as selected by Shimanouchi³² and those computed by Kambanis et al.¹⁹ at the MP2/3-

TABLE 5: Vibrational Frequencies^a and Moments of Inertia of the Bromomethyl Radicals

moments of inertia ^b	observed ^c	ref 19 ^d	this work ^e	IR intensity ^f
CH ₂ Br [•]				
0.030 57		3538.4	3140, A''	0.10
0.759 24		3356.3	3004, A'	12.37
0.787 53	1356	1462.3	1359, A'	46.62
	953	969.9	903, A''	1.21
	693	677.0	639, A'	22.08
	368	133.8	455, A'	46.75
CHBr ₂ [•]				
0.224 51		3459.3	3070, A'	1.53
6.888 21	1164	1256.3	1157, A''	98.12
7.099 99	778	780.4	735, A''	98.37
	633	610.2	586, A'	10.99
		392.2	472, A'	14.76
		186.6	172, A'	0.11
CBr ₃ [•]				
6.795 28	773	821.7, 818.3	768, E	101.93
6.795 28		302.3	309, A ₁	0.06
13.5598		183.0	208, A ₁	0.10
		164.8, 164.3	151, E	0.12

^a Units: cm⁻¹. ^b I_a, I_b, I_c; units: 10⁻³⁸ g cm². ^c Taken from ref 35. ^d Calculated at the HF/3-21++G** level without any symmetry constraints and subsequently scaled by 0.89. ^e Calculated at the HF/6-31G* level and subsequently scaled by 0.8953. ^f Intensity is calculated by the atomic polar method as implemented in GAUSSIAN 92, in kilometers per mole.

21++G** level without symmetry constraints. Examination of Table 4 reveals that the 6-31G* basis set has once again given better results. Even upon scaling, the frequencies with the 3-21++G** basis set are too large at the high end of the spectrum and too small for the low-frequency fundamentals. Scott and Radom³¹ derived from a least-squares fit a frequency scaling factor for the 3-21G basis set of 0.9085, but it is clear that even if this factor had been used as opposed to the widely used factor of 0.8929, the agreement would not have been any better. It is of interest to note that our calculated frequencies are in even better agreement with recent matrix isolation infrared spectroscopic measurements of Nielsen and co-workers^{33,34} (values given in parentheses in column 2 of Table 4). This is particularly true for CH₂Br₂.

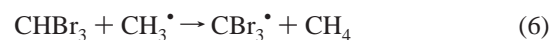
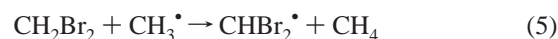
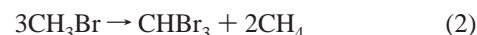
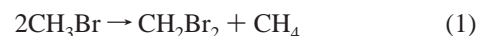
Bromomethyl Radicals. Vibrational frequencies, IR intensities, and moments of inertia are listed in Table 5 along with comparison to the HF/3-21++G** theoretical frequencies of Kambanis et al.¹⁹ and experimentally measured frequencies from matrix isolation infrared spectroscopic studies tabulated by Jacox.³⁵ The experimentally observed spectra for these radicals are incomplete, but where comparison is possible our results compare quite favorably, particularly for the strongest fundamentals. A similar trend as was observed with the molecules is seen here with the 3-21++G** results: overestimation of the high-frequency fundamentals.

III. Thermodynamic Properties. Previous work has demonstrated the reliability of calculating the heat of formation of both molecules^{36,37} and radicals³⁸⁻⁴⁴ by coupling ab initio theoretically computed energy changes for homodesmic and isodesmic reactions with known heats of formation of other reaction components. As was mentioned earlier, the standard enthalpies of formation of the bromomethanes and bromomethyl radicals are not well established with the exception of methyl bromide. With this in mind we selected the following six homodesmic reactions to afford calculation of the heat of formation of all other brominated species:

TABLE 6: Theoretical Reaction Energies (ΔE), Zero-Point Energy Corrections ($\Delta(ZPE)$), Reaction Enthalpies ($\Delta H^\circ_{f,0}(\text{Rx})$), and Heats of Formation ($\Delta H^\circ_{f,0}$), at 0 K^a

species	isodesmic reaction no. ^b	ΔE^c	$\Delta(ZPE)^d$	$\Delta H^\circ_{f,0}(\text{Rx})^e$	$\Delta H^\circ_{f,0}^f$
CH ₂ Br ₂	1	1.37	-0.89	0.48	6.17
CHBr ₃	2	4.44	-2.59	1.85	18.38
CBr ₄	3	9.78	-4.82	4.95	32.33
CH ₂ Br [•]	4	-2.99	0.63	-2.37	44.18
CHBr ₂ [•]	5	-6.88	1.16	-5.72	52.15
CBr ₃ [•]	6	-11.26	1.70	-9.57	60.51

^a All values are given in kilocalories per mole. ^b See isodesmic reaction number in the text. ^c Evaluated at the MP4/6-31G**/MP2/6-31G* level. ^d Scaled by 0.8929. ^e $\Delta H^\circ_{f,0}(\text{Rx}) = \Delta E + \Delta(ZPE)$. ^f From computed $\Delta H^\circ_{f,0}(\text{Rx})$ and known heats of formation of other species in the isodesmic reactions.



As both methane and the methyl radical appear in these reactions, the total electronic energies and zero point energies were determined at the same level of theory; numerical values appear in Table 2.

The first three reactions require knowledge of the heat of formation of methyl bromide (and thus it is the "seed" value for the other bromomethanes) and methane. After a careful and extensive review of the literature, we chose the standard enthalpy of formation at 0 K ($\Delta H^\circ_{f,0}$) for methyl bromide to be -5.15 kcal/mol, based on an arithmetic average of the selected values (in kilocalories per mole) appearing in the following four standard compendia: (a) Kudchadker and Kudchadker,¹⁵ -5.34; (b) Gurvich et al.,⁴⁵ -5.02; (c) Wagman et al.,⁴⁶ -4.74; and (d) Lias et al.,⁴⁷ -5.5. The standard enthalpy of formation for methane at 0 K was calculated from spectroscopic data³² to be -15.99 ± 0.08 kcal/mol from the tabulated value at 298 K of -17.895 ± 0.08 kcal/mol in the JANAF thermochemical tables.⁴⁸ From these two selected heats of formation along with calculated theoretical reaction enthalpies [$\Delta H^\circ_{f,0}(\text{Rx})$], the standard enthalpies of formation at 0 K for CH₂Br₂, CHBr₃, and CBr₄ were determined, the results of which are presented in Table 6. It should be noted that the theoretical reaction energies (ΔE) were corrected with computed zero-point vibrational energy corrections that had been scaled by 0.8929.

Calculation of the standard enthalpy of formation of the bromomethyl radicals as appearing in isodesmic reactions 4-6 required input of the standard enthalpy of formation of one of the bromomethanes generated in the first three reactions and that of the methyl radical. We calculated $\Delta H^\circ_{f,0}(\text{CH}_3^\bullet)$ to be 35.7 ± 0.1 kcal/mol from $\Delta H^\circ_{f,298}(\text{CH}_3^\bullet) = 35.1 \pm 0.1$ kcal/mol as measured by Heneghan et al.⁴⁹ The resulting theoretically estimated standard enthalpies of formation at 0 K for CH₂Br[•], CHBr₂[•], and CBr₃[•] are listed in Table 6.

Ideal gas thermodynamic functions C_p° , S° , $-(G^\circ - H^\circ_0)/T$, and $H^\circ - H^\circ_0$ in the temperature range 0-1500 K and 1 atm of pressure were calculated for all molecules and radicals by

TABLE 7: Ideal Gas Thermodynamic Properties for CH₃Br^a

T (K)	C _p ^o (cal K ⁻¹ mol ⁻¹)	S ^o (cal K ⁻¹ mol ⁻¹)	-(G ^o - H ^o ₀)/T (cal K ⁻¹ mol ⁻¹)	H ^o - H ^o ₀ (kcal mol ⁻¹)	ΔH _f ^o (kcal mol ⁻¹)	ΔG _f ^o (kcal mol ⁻¹)	log K _f
0	0.0	0.0	0.0	0.0	-5.15 ^b	-5.15	-∞
100	7.99	49.32	41.36	0.80	-5.84	-6.45	14.10
200	8.75	55.03	46.91	1.62	-6.58	-6.80	7.43
298.15	10.24	58.78	50.22	2.55	-8.82	-6.56	4.81
300	10.27	58.84	50.28	2.57	-8.84	-6.54	4.77
400	12.00	62.04	52.83	3.68	-13.13	-4.93	2.69
500	13.61	64.89	54.96	4.97	-13.66	-2.81	1.23
600	15.01	67.50	56.83	6.40	-14.10	-0.60	0.22
700	16.23	69.91	58.53	7.96	-14.46	1.68	-0.52
800	17.29	72.15	60.10	9.64	-14.75	4.00	-1.09
900	18.23	74.24	61.55	11.42	-14.97	6.36	-1.54
1000	19.05	76.20	62.92	13.28	-15.14	8.74	-1.91
1100	19.77	78.05	64.21	15.22	-15.26	11.13	-2.21
1200	20.40	79.80	65.44	17.23	-15.34	13.54	-2.47
1300	20.95	81.45	66.61	19.30	-15.39	15.95	-2.68
1400	21.43	83.02	67.72	21.42	-15.41	18.36	-2.87
1500	21.85	84.52	68.79	23.59	-15.41	20.77	-3.03

^a C_p^o, -(G^o - H^o₀)/T, and H^o - H^o₀ were calculated from vibrational frequencies by using an HF/6-31G* basis set for C and H and a general basis set for Br (see text). ^b Selected mean seed value (see text).

TABLE 8: Ideal Gas Thermodynamic Properties for CH₂Br₂^a

T (K)	C _p ^o (cal K ⁻¹ mol ⁻¹)	S ^o (cal K ⁻¹ mol ⁻¹)	-(G ^o - H ^o ₀)/T (cal K ⁻¹ mol ⁻¹)	H ^o - H ^o ₀ (kcal mol ⁻¹)	ΔH _f ^o (kcal mol ⁻¹)	ΔG _f ^o (kcal mol ⁻¹)	log K _f
0	0.0	0.0	0.0	0.0	6.17 ^b	6.17	-∞
100	9.29	58.50	50.06	0.84	5.57	3.47	-7.58
200	11.04	65.43	56.16	1.85	4.73	1.67	-1.83
298.15	13.13	70.23	60.03	3.04	1.07	0.69	-0.51
300	13.17	70.31	60.09	3.06	1.05	0.69	-0.50
400	15.08	74.37	63.17	4.48	-6.72	2.15	-1.17
500	16.63	77.91	65.77	6.07	-7.03	4.40	-1.92
600	17.87	81.05	68.06	7.80	-7.27	6.71	-2.44
700	18.86	83.88	70.12	9.63	-7.45	9.05	-2.83
800	19.70	86.46	72.00	11.56	-7.58	11.42	-3.12
900	20.40	88.82	73.74	13.57	-7.67	13.80	-3.35
1000	21.01	91.00	75.36	15.64	-7.72	16.19	-3.54
1100	21.54	93.03	76.88	17.77	-7.75	18.58	-3.69
1200	21.99	94.92	78.30	19.95	-7.74	20.98	-3.82
1300	22.39	96.70	79.65	22.17	-7.72	23.37	-3.93
1400	22.73	98.37	80.93	24.42	-7.68	25.76	-4.02
1500	23.03	99.95	82.14	26.71	-7.63	28.15	-4.10

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 1 (see text).

standard methods of statistical thermodynamics based on the rigid rotor harmonic oscillator model. The results are tabulated in Tables 7–13. We note that while similar tables have been published for the molecules (see ref 15 for example), this is the first time for this information to be presented in the literature for the bromomethyl radicals.

Discussion

As the primary purpose of this study has been to determine a complete thermochemical database for the CH_{4-n}Br_n bromomethanes and the corresponding CH_{3-m}Br_m bromomethyl radicals, a comparison to existing data is warranted. We state at the onset that the very good agreement between the computed structural parameters and vibrational frequencies with experimental values lends credence to the computed thermodynamic functions.

As the calculated ideal thermodynamic functions are based on the computed enthalpy of formation of each species, we have collected our computed ΔH_{f,298}^o together for comparison with a number of literature sources^{15,45,50,53,55–57} and presented them in Table 14. We start by pointing out that the reported uncertainties in the heats of formation are based on the cumulative uncertainties of CH₃Br, CH₄, and CH₃[•], which are 0.4, 0.08, and 0.1 kcal/mol, respectively.

Our computed heats of formation for CH₂Br₂, CHBr₃, and CBr₄ agree most closely with those of Papina, Kolesov, and Golovanova.⁵⁰ They measured ΔH_{f,298}^o(CHBr₃,g) = 13.2 ± 0.8 kcal/mol by bomb calorimetry and combined this value with the heat of formation difference ΔH_f^o(CBr₄,g) - ΔH_f^o(CHBr₃,g) = 14.4 ± 0.7 kcal/mol measured by King, Golden, and Benson⁵¹ to obtain ΔH_f^o(CBr₄,g) = 27.7 ± 0.93 kcal/mol. Papina et al.⁵⁰ then implemented these values to estimate ΔH_{f,298}^o(CH₂-Br₂,g) = 1.36 ± 1.2 kcal/mol by using a modified Bernstein scheme.⁵² It is interesting to note that relatively good agreement also exists with the selected values listed in the enormous compilation of Gurvich et al.,⁴⁵ all of our values being within the assigned uncertainties of their values. There is substantial disagreement between our theoretical heats of formation and those of Bickerton, Minas Da Piedade, and Pilcher.⁵³ They measured ΔH_f^o(CBr₄,g) = 20.05 ± 0.81 kcal/mol by rotating bomb calorimetry and then applied the Allen bond-energy scheme⁵⁴ with the heats of formation of CH₄, CH₃Br, and CBr₄ along with the enthalpy difference of King et al.⁵¹ to arrive at ΔH_f^o(CHBr₃,g) = 5.7 ± 1.0 kcal/mol and ΔH_{f,298}^o(CH₂Br₂,g) = -2.65 ± 1.2 kcal/mol. The reason for the large difference (>7.5 kcal/mol) in the values of Papina et al.⁵⁰ and those of Bickerton et al.⁵³ is not apparent. Bickerton et al.⁵³ argued that combustion calorimetry is not suitable for CHBr₃ because of

TABLE 9: Ideal Gas Thermodynamic Properties for CHBr₂^a

<i>T</i> (K)	C_p° (cal K ⁻¹ mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)	$-(G^\circ - H^\circ_0)/T$ (cal K ⁻¹ mol ⁻¹)	$H^\circ - H^\circ_0$ (kcal mol ⁻¹)	ΔH°_f (kcal mol ⁻¹)	ΔG°_f (kcal mol ⁻¹)	log K_f
0	0.0	0.0	0.0	0.0	18.38 ^b	18.38	∞
100	11.74	65.18	55.79	0.94	17.92	14.58	-31.85
200	14.73	74.29	62.94	2.27	17.12	11.53	-12.59
298.15	17.03	80.62	67.76	3.83	12.16	9.45	-6.93
300	17.07	80.73	67.84	3.87	12.13	9.44	-6.88
400	18.82	85.89	71.73	5.66	0.98	10.82	-5.91
500	20.09	90.23	75.01	7.61	0.93	13.29	-5.81
600	21.02	93.98	77.86	9.67	0.93	15.76	-5.74
700	21.72	97.28	80.41	11.81	0.95	18.23	-5.69
800	22.27	100.21	82.70	14.01	1.00	20.70	-5.65
900	22.72	102.86	84.80	16.26	1.06	23.16	-5.62
1000	23.10	105.28	86.73	18.55	1.14	25.61	-5.60
1100	23.41	107.49	88.52	20.88	1.22	28.05	-5.57
1200	23.68	109.54	90.18	23.23	1.32	30.49	-5.55
1300	23.91	111.45	91.75	25.61	1.42	32.91	-5.53
1400	24.11	113.23	93.22	28.01	1.53	35.33	-5.52
1500	24.28	114.90	94.61	30.43	1.64	37.74	-5.50

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 2 (see text).**TABLE 10: Ideal Gas Thermodynamic Properties for CBr₄^a**

<i>T</i> (K)	C_p° (cal K ⁻¹ mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)	$-(G^\circ - H^\circ_0)/T$ (cal K ⁻¹ mol ⁻¹)	$H^\circ - H^\circ_0$ (kcal mol ⁻¹)	ΔH°_f (kcal mol ⁻¹)	ΔG°_f (kcal mol ⁻¹)	log K_f
0	0.0	0.0	0.0	0.0	32.33 ^b	32.32	∞
100	15.29	65.27	54.43	1.08	32.05	28.12	-61.46
200	19.42	77.33	63.10	2.85	31.40	24.43	-26.70
298.15	21.71	85.55	69.20	4.88	25.23	21.82	-15.99
300	21.75	85.69	69.30	4.92	25.20	21.80	-15.88
400	23.13	92.15	74.24	7.17	10.72	23.65	-12.92
500	23.95	97.41	78.36	9.52	10.99	26.85	-11.74
600	24.46	101.82	81.91	11.95	11.26	30.00	-10.93
700	24.80	105.62	85.03	14.41	11.51	33.10	-10.33
800	25.02	108.95	87.82	16.90	11.75	36.17	-9.88
900	25.19	111.90	90.33	19.41	11.98	39.21	-9.52
1000	25.30	114.56	92.63	21.94	12.20	42.22	-9.23
1100	25.39	116.98	94.73	24.47	12.41	45.21	-8.98
1200	25.46	119.19	96.68	27.01	12.61	48.19	-8.78
1300	25.51	121.23	98.49	29.56	12.80	51.14	-8.60
1400	25.56	123.13	100.18	32.12	12.99	54.09	-8.44
1500	25.59	124.89	101.77	34.67	13.16	57.01	-8.31

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 3 (see text).**TABLE 11: Ideal Gas Thermodynamic Properties for CH₂Br^a**

<i>T</i> (K)	C_p° (cal K ⁻¹ mol ⁻¹)	S° (cal K ⁻¹ mol ⁻¹)	$-(G^\circ - H^\circ_0)/T$ (cal K ⁻¹ mol ⁻¹)	$H^\circ - H^\circ_0$ (kcal mol ⁻¹)	ΔH°_f (kcal mol ⁻¹)	ΔG°_f (kcal mol ⁻¹)	log K_f
0	0.0	0.0	0.0	0.0	44.18 ^b	44.18	∞
100	8.09	52.05	44.08	0.80	43.87	41.77	-91.28
200	9.39	58.01	49.69	1.66	43.47	39.81	-43.50
298.15	10.88	62.04	53.12	2.66	41.63	38.27	-28.05
300	10.90	62.11	53.18	2.68	41.62	38.25	-27.86
400	12.11	65.42	55.84	3.83	37.71	37.92	-20.72
500	13.04	68.23	58.04	5.09	37.52	37.99	-16.60
600	13.78	70.67	59.95	6.44	37.34	38.10	-13.88
700	14.41	72.85	61.64	7.85	37.17	38.24	-11.94
800	14.95	74.81	63.16	9.32	37.03	38.40	-10.49
900	15.44	76.60	64.56	10.84	36.90	38.58	-9.37
1000	15.88	78.25	65.85	12.40	36.79	38.78	-8.47
1100	16.27	79.78	67.04	14.01	36.70	38.98	-7.74
1200	16.62	81.21	68.17	15.66	36.62	39.19	-7.14
1300	16.94	82.55	69.22	17.33	36.56	39.41	-6.63
1400	17.21	83.82	70.22	19.04	36.50	39.63	-6.19
1500	17.46	85.02	71.17	20.78	36.45	39.85	-5.81

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 4 (see text).

decomposition of the sample during measurement. In a previous critical examination of kinetic and thermochemical data, Tschuikow-Roux and Paddison⁵⁵ recommended the adoption of the heats of formation of Bickerton et al.,⁵³ however, as a result of the present theoretical study we now have greater confidence in the work of Papina et al.⁵⁰

In Table 14 we have also made a comparison of our computed heats of formation for the bromomethyl radicals with selected values of McMillen and Golden,⁵⁶ with those from a monoenergetic electron impact study of Holmes and Lossing,⁵⁷ and with derived values from the review of Tschuikow-Roux and Paddison.⁵⁵ Our theoretically derived $\Delta H^\circ_{f,298}(\text{CH}_2\text{Br}^\bullet) = 41.63$

TABLE 12: Ideal Gas Thermodynamic Properties for CHBr_2^{a}

T (K)	C_p° (cal K^{-1} mol $^{-1}$)	S° (cal K^{-1} mol $^{-1}$)	$-(G^\circ - H^\circ_0)/T$ (cal K^{-1} mol $^{-1}$)	$H^\circ - H^\circ_0$ (kcal mol $^{-1}$)	ΔH°_f (kcal mol $^{-1}$)	ΔG°_f (kcal mol $^{-1}$)	$\log K_f$
0	0.0	0.0	0.0	0.0	52.15 ^b	52.15	∞
100	9.31	60.85	52.43	0.84	51.93	48.37	-105.70
200	11.39	67.93	58.55	1.87	50.67	45.00	-49.18
298.15	13.21	72.83	62.48	3.09	48.11	42.30	-31.01
300	13.24	72.91	62.54	3.11	48.09	42.27	-30.79
400	14.55	76.91	65.65	4.50	40.65	41.85	-22.87
500	15.45	80.26	68.25	6.01	40.61	42.16	-18.43
600	16.09	83.14	70.49	7.58	40.57	42.47	-15.47
700	16.58	85.65	72.48	9.22	40.53	42.79	-13.36
800	16.98	87.90	74.27	10.90	40.50	43.11	-11.78
900	17.31	89.92	75.90	12.61	40.48	43.44	-10.55
1000	17.60	91.75	77.39	14.36	40.46	43.77	-9.57
1100	17.84	93.44	78.78	16.13	40.44	44.10	-8.76
1200	18.05	95.00	80.07	17.93	40.43	44.44	-8.09
1300	18.24	96.46	81.27	19.74	40.42	44.77	-7.53
1400	18.40	97.81	82.41	21.57	40.41	45.11	-7.04
1500	18.54	99.09	83.48	23.42	40.41	45.44	-6.62

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 5 (see text).

TABLE 13: Ideal Gas Thermodynamic Properties for CBr_3^{a}

T (K)	C_p° (cal K^{-1} mol $^{-1}$)	S° (cal K^{-1} mol $^{-1}$)	$-(G^\circ - H^\circ_0)/T$ (cal K^{-1} mol $^{-1}$)	$H^\circ - H^\circ_0$ (kcal mol $^{-1}$)	ΔH°_f (kcal mol $^{-1}$)	ΔG°_f (kcal mol $^{-1}$)	$\log K_f$
0	0.0	0.0	0.0	0.0	60.51 ^b	60.51	∞
100	12.15	65.30	55.81	0.95	60.44	55.86	-122.10
200	15.06	74.75	63.11	2.33	59.99	51.45	-56.22
298.15	16.67	81.08	68.03	3.89	55.36	47.36	-35.08
300	16.70	81.18	68.11	3.92	55.34	47.82	-34.83
400	17.72	86.14	72.02	5.65	44.46	47.55	-25.98
500	18.36	90.17	75.26	7.45	44.62	48.31	-21.11
600	18.76	93.55	78.04	9.31	44.77	49.03	-17.86
700	19.03	96.47	80.47	11.20	44.89	49.73	-15.53
800	19.21	99.02	82.63	13.11	45.00	50.41	-13.77
900	19.34	101.29	84.58	15.04	45.10	51.08	-12.40
1000	19.44	103.33	86.35	16.98	45.18	51.74	-11.31
1100	19.51	105.19	87.98	18.93	45.25	52.39	-10.41
1200	19.56	106.89	89.49	20.88	45.31	53.04	-9.66
1300	19.61	108.46	90.89	22.84	45.37	53.69	-9.03
1400	19.64	109.91	92.20	24.80	45.41	54.32	-8.48
1500	19.67	111.27	93.42	26.77	45.45	54.96	-8.01

^a See footnote to Table 7. ^b Assigned on the basis of isodesmic reaction 6 (see text).

± 0.4 kcal/mol is in good agreement with all the cited values in the literature, particularly so with the value (41.5 kcal/mol) selected by McMillen and Golden.⁵⁶ This value may be traced back to the critical analysis of Furuyama, Golden, and Benson⁵⁸ of the much earlier kinetic data of Kistiakowsky and Van Artsdalen⁵⁹ and subsequent correction of Fettis and Trotman-Dickenson.⁶⁰ It is quite surprising to see such agreement with experimental measurements taken more than half a century ago!

There is considerably greater discrepancy in the reported heat of formation for the dibromomethyl radical. The computed $\Delta H^\circ_{f,298}(\text{CHBr}_2^\bullet) = 48.11 \pm 0.6$ kcal/mol of this study is in closest agreement with the calculated value (45.0 ± 2 kcal/mol) of Tschuikow-Roux and Paddison.⁵⁵ This is somewhat surprising in view of their adoption of the heats of formation for the di- and tribromomethanes of Bickerton et al.⁵³ It has already been pointed out⁵⁵ that the value selected by McMillen and Golden for the heat of formation of CHBr_2^\bullet is far too high.

The large tabulation of Gurvich et al.⁴⁵ lists a heat of formation for only the tribromomethyl radical, and this is in very good agreement with our computed $\Delta H^\circ_{f,298}(\text{CBr}_3^\bullet) = 55.36 \pm 0.7$ kcal/mol. Holmes and Lossing⁵⁷ is the only source giving heats of formation for all three bromomethyl radicals, and their values are all lower than our computed values.

From our computed standard enthalpies of formation at 298 K we calculated C–H and C–Br bond dissociation energies for the bromomethanes. These are compared with available experimental or calculated published values^{51,55,56,61} and those computed by Kambanis et al.¹⁹ Examination of Table 15 reveals that our calculated bond dissociation energies (DH°) are generally in very good agreement with available literature values. The derived C–H bond dissociation energies show the well-accepted trend of decreasing bond strength with bromine substitution, a trend that is also observed with chlorine substitution but just the opposite of which is seen with fluorine substitution.^{55,56,62,63} There is some difference in our derived C–Br bond dissociation energies for CH_2Br_2 and CHBr_3 from values reported in the literature, with our values being lower by approximately 2 and 3 kcal/mol, respectively. The derived $DH^\circ(\text{CH}_2\text{Br}-\text{Br}) = 69.8 \pm 2$ kcal/mol by Tschuikow-Roux and Paddison⁵⁵ is too high because, as pointed out earlier, they adopted the estimated $\Delta H^\circ_{f,298}(\text{CH}_2\text{Br}_2, \text{g})$ of Bickerton et al.⁵³ Furuyama et al.⁵⁸ have already pointed out that the $DH^\circ(\text{CHBr}_2-\text{Br}) = 66 \pm 4$ kcal/mol reported by Miller and Palmer⁶¹ is too high, and in fact in their analysis adopted the minimum value of 62 kcal/mol. We have derived a value that is higher than the minimum value and well within the suggested uncertainty limits of Miller and Palmer.⁶¹ Our computed DH° -

TABLE 14: Comparison of Computed and Experimental Heats of Formation at 298 K^a

species	$\Delta H_{f,298}^{\circ}(\text{calc})^b$	$\Delta H_{f,298}^{\circ}(\text{lit.})^c$	ref
CH ₂ Br ₂	1.07 ± 0.6	1.4 ± 1.2	50
		2.39 ± 3.59	45
		-2.65 ± 1.2	53
		-3.53 ± 0.8	15
CHBr ₃	12.16 ± 0.7	13.2 ± 0.8	50
		14.34 ± 3.59	45
		5.7 ± 1.1	53
		4.0 ± 0.8	15
CBr ₄	25.23 ± 0.8	27.7 ± 0.93	50
		28.68 ± 3.59	45
		20.05 ± 0.81	53
		19.0 ± 1.0	15
CH ₂ Br*	41.63 ± 0.4	41.5	56
		40.4 ± 1	55
		40.2	57
		45.0 ± 2	55
CHBr ₂ *	48.11 ± 0.6	44.4	57
		54.3	56
		56.17 ± 5.98	45
		49.0	57
CBr ₃ *	55.36 ± 0.7		

^a Values are given in kilocalories per mole. ^b Reported uncertainty based on cumulative uncertainties in CH₃Br, CH₄, and CH₃*. ^c Selected experimental or derived values from the literature.

TABLE 15: Computed C-H and C-Br Bond Dissociation Energies in the Bromomethanes^a

bond	this work ^b	literature ^c	ref ^d	ref 19 ^e
CH ₂ Br-H	102.5 ± 0.6	102.0 ± 2	56	99.564
CHBr ₂ -H	99.1 ± 0.8	99.7 ± 1.8	55	97.282
CBr ₃ -H	95.3 ± 1.0	96.0 ± 1.6	51	94.788
CH ₃ -Br	70.7 ± 0.4	70.9 ± 0.3	55, 56	74.969
CH ₂ Br-Br	67.3 ± 0.7	69.8 ± 2	55	74.122
CHBr ₂ -Br	62.7 ± 0.9	66 ± 4	61	73.020
CBr ₃ -Br	56.9 ± 1.1	56.2 ± 1.8	51	

^a Values were determined at 298 K and are given in kilocalories per mole. ^b Determined from computed $\Delta H_{f,298}^{\circ}$ as given in Table 14 and $\Delta H_{f,298}^{\circ}(\text{H}) = 52.102 \pm 0.001$ and $\Delta H_{f,298}^{\circ}(\text{Br}) = 26.735$ kcal/mol from ref 48. Accumulated uncertainties are from derived heats of formation in Table 14. ^c Selected from available literature values, experimental or calculated. ^d Reference number for quoted literature value. ^e Determined from single point energies computed at the MP2/6-31++G** level and geometries and frequencies computed at the MP2/3-21++G** and HF/3-21++G** level.

(CBr₃-Br) = 56.9 ± 1.1 kcal/mol is in excellent agreement with the thermal bromination and transition-state theory calculations of King, Golden, and Benson⁵¹ (56.2 ± 1.8 kcal/mol).

Comparison of the bond dissociation energies calculated by Kambanis et al.¹⁹ indicate that their C-H values are all lower than both our computed energies and those found in the literature. The opposite trend is seen in their theoretical C-Br bond dissociation energies, which are all considerably higher. It should be noted that Kambanis et al.¹⁹ have calculated their C-H and C-Br bond dissociation energies without appealing to experimentally measured heats of formation and thus their approach is in some respects more direct. However, it is well-known that such a direct method usually results in substantial residual electron correlation error(s), and this is certainly seen in their results. As indicated earlier, we used isodesmic reactions coupled with the heats of formation of CH₃Br, CH₄, and CH₃* because these values are well-known from experiments with little uncertainty. Had this thermodynamic information been unavailable, one would have to use a similar approach as Kambanis et al.¹⁹ to calculate the C-H and C-Br bond dissociation energies.

This theoretical study of the bromomethanes and bromomethyl radicals has generated a self-consistent set of thermo-

dynamic information (standard enthalpies of formation and bond dissociation energies) that is in very good agreement with available literature values.

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