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Thermodynamic Properties of Bromomethanes and Bromomethyl Radicals: An *ab Initio* Study[1]

S. J. Paddison[2-4] and E. Tschuikow-Roux[2]

Thermochemical data on volatile organic compounds containing bromine are needed for atmospheric modeling, in view of their ozone depletion potential upon photodissociation and the release of atomic bromine. Yet even for the bromomethane series, with the exception of CH_3Br, thermodynamic properties are not well established. Similarly, structural and thermochemical information on brominated methyl radicals is incomplete or not available. In this paper we have adopted a computational approach to obtain this needed information. Equilibrium geometries for the molecules $CH_{4-n}Br_n$ ($n = 0$–4) and radicals $CH_{3-m}Br_m$ ($m = 0$–3) were optimized at both HF/6-31G* and MP2/6-31G* levels of theory. Moments of inertia, harmonic vibrational frequencies, and thermodynamic functions were determined at the HF/6-31G* level. Electron correlation contributions were performed by single-point calculations at both second- and 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. These data were then used in the determination of $\Delta H^\circ_{f,T}$, $\Delta G^\circ_{f,T}$, and $K_{f,T}$ for all species over the temperature range 0 to 1500 K. A comparison was made to the existing standard enthalpies of formation at 298 K, both experimentally measured and theoretically estimated, for CH_2Br_2, $CHBr_3$, CBr_4, $CH_2Br\bullet$, $CHBr_2\bullet$, and $CBr_3\bullet$.

KEY WORDS: bromomethanes; bromomethyl radicals; enthalpies of formation; thermodynamic properties.

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[2] Department of Chemistry, The University of Calgary, 2500 University Drive N.W., Calgary, Alberta T2N 1N4, Canada.

[3] Present address: Los Alamos National Laboratory, Materials Science and Technology Division, MST-11, MS D429, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

[4] To whom correspondence should be addressed.

1. INTRODUCTION

Bromine is widely present in the Earth's atmosphere and exists in a large number of forms, both natural (CH_3Br, CH_2Br_2, $CHBr_3$, CH_2BrCl, $CHBr_2Cl$) and anthropogenic (CF_3Br and CF_2BrCl) in origin [1]. Methyl bromide, the most abundant source of bromine in the troposphere [2], has recently received considerable attention [3–6]: (1) because of its high ozone depletion potential (ODP), estimated to be as high as 0.7 [7], and (2) because of evidence that its origin may be predominantly man-made [8] rather than natural as initially thought. Very recent studies on the atmospheric chemistry of dibromomethane [9, 10] have also been conducted, suggesting the importance of this molecule in possible ozone depletion.

Thermochemical data on these brominated methanes are required in the successful modeling of the effect of these compounds in upper atmosphere chemistry. Of the unmixed bromomethanes [$CH_{4-n}Br_n$ ($n = 1$–4)], only the thermodynamic properties of CH_3Br are well established [11]. In addition to the lack of experimental investigations, very few theoretical studies aimed at the determination of either structural or thermodynamic information on the bromomethanes have been undertaken; the only published results are those for methyl bromide at a very low level of theory [12–14].

With the recognition of the importance of several of these molecules in elucidating the atmospheric thermochemistry, we present in this paper the results of an *ab initio* study of the entire series of brominated methanes with extension to include the corresponding bromomethyl radicals [$CH_{3-m}Br_m$ ($m = 1$–3)].

The standard thermodynamic functions of enthalpy, free energy, entropy, and heat capacity are tabulated as a function of temperature on the basis of vibrational frequencies (experimental when available, theoretical otherwise), calculated moments of inertia, and computed total energies. From a series of related isodesmic reactions with a selected "seed" value for the standard enthalpy of formation of methyl bromide, the heats of formation for the other bromomethanes and the bromomethyl radicals are evaluated. Finally, a comparison is made with available experimental or empirically estimated values.

2. METHOD

Standard *ab initio* molecular orbital calculations were carried out with the GAUSSIAN 92 system of programs [15]. Singlet states ($CH_{4-n}Br_n$ molecules) were calculated using closed-shell Hartree–Fock theory (RHF) [16] and doublet states ($CH_{3-m}FBr_m$ radicals) using Pople–Nesbet spin unrestricted theory (UHF) [17]. The internal 6-31G* basis set [18] 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. [19], an alternative originally proposed and tested with favorable results by McGrath and Radom [20], 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 [21]. 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. Vibrational frequencies and zero point energies were obtained at the HF/6-31G* level using analytical second derivatives [22], and the results then uniformly scaled by 0.89 to adjust for systematic overestimation of the values at the HF-SCF level [23].

3. RESULTS AND DISCUSSION

3.1. Geometries and Frequencies

The full details of our results for the optimized structures of both the molecules and the radicals are presented elsewhere [24]. Suffice it to comment, however, that very little difference was observed in the geometries refined at the MP2 level with those computed at the HF-SCF level. In addition, comparison of the theoretical geometries with experimentally measured structures [11] reveals very good agreement; observed trends being (1) the carbon–hydrogen bond lengths were slightly shorter in the computed structures, and (2) the calculated carbon–bromine bond distances slightly longer than those determined from microwave measurements. We note that no experimentally measured geometrical parameters are reported for any of the bromomethyl radicals.

Upon uniform scaling of the calculated vibrational frequencies, the comparison with observed fundamental frequencies in the molecules [25] is very favorable. Jacox [26] has measured, by infrared matrix isolation techniques, and tabulated some of the frequencies for the bromomethyl radicals, and the agreement with our computed frequencies is generally quite good. We have presented a complete set of vibrational frequencies for the radicals, heretofore unavailable, along with computed IR intensities and corresponding moments of inertia; the complete details of which the reader is again referred to our companion paper [24]. These computed harmonic frequencies and moments of inertia for both the molecules and the radicals were used in the calculation of zero-point energies and thermodynamic functions.

3.2. Energetics and Thermodynamic Properties

The total energies and zero-point energies (ZPE) for all the brominated species are listed in Table I. Calculations were also performed for methane and the methyl radical. Energies are reported at both the MP2/6-31G* and the MP4/6-31G** levels based on MP2/6-31G* optimized structures; energies at the higher electron correlation level are approximately 0.05 Hartree lower. The MP4/6-31G** single-point energies along with the ZPEs were used to compute the reaction enthalpies for the following isodesmic reactions:

$$2CH_3Br \rightarrow CH_2Br_2 + CH_4 \tag{1}$$

$$3CH_3Br \rightarrow CHBr_3 + 2CH_4 \tag{2}$$

$$4CH_3Br \rightarrow CBr_4 + 3CH_4 \tag{3}$$

$$CH_3Br + CH_3\bullet \rightarrow CH_2Br\bullet + CH_4 \tag{4}$$

$$CH_2Br_2 + CH_3\bullet \rightarrow CHBr_2\bullet + CH_4 \tag{5}$$

$$CHBr_3 + CH_3\bullet \rightarrow CBr_3\bullet + CH_4 \tag{6}$$

The first three reactions require knowledge of the heat of formation of methyl bromide 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 -21.55 kJ $\cdot$ mol^{-1} based on an arithmetic average of the selected values appearing in the following four standard compendia: (a) Kudchadker and Kudchadker [11], -22.34; (b) Gurvich et al. [27], -21.00; (c) Wagman et al. [28], -19.83; and (d) Lias et al. [29], -23.01 kJ $\cdot$ mol^{-1}. The standard enthalpy of formation for methane at 0 K was calculated from spectroscopic data [25] to be -66.90 ± 0.33 kJ $\cdot$ mol^{-1} from the tabulated value at 298 K of -75.25 ± 0.33 kJ $\cdot$ mol^{-1} in the JANAF thermochemical tables [30]. From these two selected heats of formation along with calculated theoretical reaction enthalpies [$\Delta H^{\circ}_0(Rx)$], the standard enthalpy of formation at 0 K for CH_2Br_2, $CHBr_3$, and CBr_4 were determined, the results of which are presented in Table II. Calculation of the standard enthalpy of formation of the bromomethyl radicals as appearing in isodesmic reactions [Eqs. (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 $\Delta H^{\circ}_{f,0}(CH_3\bullet)$ to be 149.41 ± 0.42 kJ $\cdot$ mol^{-1} from $\Delta H^{\circ}_{f,298}(CH_3\bullet) = 146.86 \pm 0.42$ kJ $\cdot$ mol^{-1} as measured by Heneghan et al. [31]. The resulting theoretically estimated standard enthalpies of formation for $CH_2Br\bullet$, $CHBr_2\bullet$, and $CBr_3\bullet$ are listed in Table II.

Table I. 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*)
CH4	−40.33255	−40.38864	125.5
CH_3Br	−2610.00866	−2610.06460	105.0
CH_2Br_2	−5179.68265	−5179.73838	80.3
$CHBr_3$	−7749.35392	−7749.40944	51.9
CBr_4	−10319.02126	−10319.07690	20.9
$CH_3\bullet$	−39.66875	−39.71475	81.2
$CH_2Br\bullet$	−2609.34887	−2609.39548	63.6
$CHBr_2\bullet$	−5179.02863	−5179.07545	41.4
$CBr_3\bullet$	−7748.70664	−7748.75350	15.5

[a] Total energies in Hartrees.

[b] Unscaled zero-point vibrational energies in $\mathrm{kJ \cdot mol^{-1}}$.

Ideal-gas thermodynamic functions C°_p, S°, $-(G^\circ - H^\circ_0)/T$, and $H^\circ - H^\circ_0$ in the temperature range 0 to 1500 K and at 1 atm of pressure (101.3 kPa) were calculated by standard methods of statistical thermodynamics based on the rigid rotor harmonic oscillator model. Experimental frequencies were used in the calculations involving the molecules and theoretical frequencies were used for the radicals. The results are listed in Tables III–IX.

Table II. Theoretical Reaction Energies, ΔE; Zero-Point Energy Corrections, Δ(ZPE); Reaction Enthalpies, ΔH°_0(Rx); and Heats of Formation, $\Delta H^\circ_{f,0}$, at 0 K[a]

Species	Isodesmic reaction No.[b]	ΔE^c	$\Delta(\mathrm{ZPE})^d$	$\Delta H^\circ_0(\mathrm{Rx})^e$	$\Delta H^{\circ f}_{f,0}$
CH_2Br_2	1	5.73	−3.72	2.01	25.82
$CHBr_3$	2	18.58	−10.84	7.74	76.90
CBr_4	3	40.92	−20.17	20.71	135.27
$CH_2Br\bullet$	4	−12.51	2.64	−9.92	184.85
$CHBr_2\bullet$	5	−28.79	4.85	−23.93	218.20
$CBr_3\bullet$	6	−47.11	7.11	−40.04	253.17

[a] All values in $\mathrm{kJ \cdot mol^{-1}}$.

[b] See isodesmic reaction No. in the text.

[c] Evaluated at the MP4/6-31G**//MP2/6-31G* level.

[d] Scaled by 0.8929.

[e] $\Delta H^\circ_0(\mathrm{Rx}) = \Delta E + \Delta(\mathrm{ZPE})$.

[f] From computed ΔH°_0(Rx) and known heats of formation of other species in the isodesmic reactions.

Table III. Ideal-Gas Thermodynamic Properties for CH_3Br[a]

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	($J \cdot mol^{-1} \cdot K^{-1}$)			($kJ \cdot mol^{-1}$)			
0	0.0	0.0	0.0	0.0	−21.55[b]	−21.55	$-\infty$
100	33.43	206.35	173.05	3.35	−24.43	−26.99	58.99
200	36.61	230.25	196.27	6.78	−27.53	−28.45	31.09
298.15	42.84	245.94	210.12	10.67	−36.90	−27.45	20.13
300	42.97	246.19	210.37	10.75	−36.99	−27.36	19.96
400	50.21	259.58	221.04	15.40	−54.94	−20.63	11.25
500	56.94	271.50	229.95	20.79	−57.15	−11.76	5.15
600	62.80	282.42	237.78	26.78	−58.99	−2.51	0.92
700	67.91	292.50	244.89	33.30	−60.50	7.03	−2.18
800	72.34	301.88	251.46	40.33	−61.71	16.74	−4.56
900	76.27	310.62	257.53	47.78	−62.63	26.61	−6.44
1000	79.71	318.82	263.26	55.56	−63.35	36.57	−7.99
1100	82.72	326.56	268.65	63.68	−63.85	46.57	−9.25
1200	85.35	333.88	273.80	72.09	−64.18	56.65	−10.33
1300	87.65	340.79	278.70	80.75	−64.39	66.73	−11.21
1400	89.66	347.36	283.34	89.62	−64.48	76.82	−12.01
1500	91.42	353.63	287.82	98.70	−64.48	86.90	−12.68

[a] C_p°, $-(G^\circ - H_0^\circ)/T$, and $H^\circ - H_0^\circ$ were calculated from vibrational frequencies 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 IV. Ideal-Gas Thermodynamic Properties for CH_2Br_2[a]

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	($J \cdot mol^{-1} \cdot K^{-1}$)			($kJ \cdot mol^{-1}$)			
0	0.0	0.0	0.0	0.0	25.82[b]	25.85	$-\infty$
100	38.87	244.8	209.5	3.52	23.30	14.52	−31.71
200	46.19	273.8	235.0	7.74	19.79	6.99	−7.66
298.15	54.94	293.8	251.2	12.72	4.48	2.89	−2.13
300	55.10	294.2	251.4	12.80	4.39	2.89	−2.09
400	63.09	311.2	264.3	18.74	−28.12	9.00	−4.90
500	69.58	326.0	275.2	25.40	−29.41	18.41	−8.03
600	74.77	339.1	284.8	32.64	−30.42	28.07	−10.21
700	78.91	351.0	293.4	40.29	−31.17	37.87	−11.84
800	82.42	361.7	301.2	48.37	−31.71	47.78	−13.05
900	85.35	371.6	308.5	56.78	−32.09	57.74	−14.02
1000	87.91	380.7	315.3	65.44	−32.30	67.74	−14.81
1100	90.12	389.2	321.7	74.35	−32.43	77.74	−15.44
1200	92.01	397.1	327.6	83.47	−32.38	87.78	−15.98
1300	93.68	404.6	333.3	92.76	−32.30	97.78	−16.44
1400	95.10	411.6	338.6	102.2	−32.13	107.8	−16.82
1500	96.36	418.2	343.7	111.8	−31.92	117.8	−17.15

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (1)] (see text).

Table V. Ideal-Gas Thermodynamic Properties for $CHBr_3$[a]

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	$(J \cdot mol^{-1} \cdot K^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.0	0.0	0.0	0.0	76.90[b]	76.90	$-\infty$
100	49.12	272.7	233.4	3.93	74.98	61.00	−133.3
200	61.63	310.8	263.3	9.50	71.63	48.24	−52.68
298.15	71.25	337.3	283.5	16.02	50.88	39.54	−29.00
300	71.42	337.8	283.8	16.19	50.75	39.50	−28.79
400	78.74	359.4	300.1	23.68	4.10	45.27	−24.73
500	84.06	377.5	313.8	31.84	3.89	55.61	−24.31
600	87.95	393.2	325.8	40.46	3.89	65.94	−24.02
700	90.88	407.0	336.4	49.41	3.98	76.27	−23.81
800	93.18	419.3	346.0	58.62	4.18	86.61	−23.64
900	95.06	430.4	354.8	68.03	4.44	96.90	−23.51
1000	96.65	440.5	362.9	77.61	4.77	107.2	−23.43
1100	97.95	449.7	370.4	87.36	5.10	117.4	−23.30
1200	99.08	458.3	377.3	97.19	5.52	127.6	−23.22
1300	100.0	466.3	383.9	107.2	5.94	137.7	−23.14
1400	100.9	473.8	390.0	117.2	6.40	147.8	−23.10
1500	101.6	480.7	395.8	127.3	6.86	157.9	−23.01

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (2)] (see text).

Table VI. Ideal-Gas Thermodynamic Properties for CBr_4[a]

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	$(J \cdot mol^{-1} \cdot K^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.0	0.0	0.0	0.0	135.3[b]	135.3	$-\infty$
100	63.97	273.1	227.7	4.52	134.1	117.7	−257.1
200	81.25	323.5	264.0	11.92	131.4	102.2	−111.7
298.15	90.83	357.9	289.5	20.42	105.6	91.29	−66.90
300	91.00	358.5	290.0	20.59	105.4	91.21	−66.44
400	96.78	385.6	310.6	30.00	44.85	98.95	−54.06
500	100.2	407.6	327.9	39.83	45.98	112.3	−49.12
600	102.3	426.0	342.7	50.00	47.11	125.5	−45.73
700	103.8	441.9	355.8	60.29	48.16	138.5	−43.22
800	104.7	455.8	367.4	70.71	49.16	151.3	−41.34
900	105.4	468.2	377.9	81.21	50.12	164.1	−39.83
1000	105.9	479.3	387.6	91.80	51.04	176.6	−38.62
1100	106.2	489.4	396.4	102.4	51.92	189.2	−37.57
1200	106.5	498.7	404.5	113.0	52.76	201.6	−36.74
1300	106.7	507.2	412.1	123.7	53.56	214.0	−35.98
1400	106.9	515.2	419.2	134.4	54.35	226.3	−35.31
1500	107.1	522.5	425.8	145.1	55.06	238.5	−34.77

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (3)] (see text).

Table VII. Ideal-Gas Thermodynamic Properties for $CH_2Br\bullet$[a]

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	$(J\cdot mol^{-1}\cdot K^{-1})$			$(kJ\cdot mol^{-1})$			
0	0.0	0.0	0.0	0.0	184.8[b]	184.8	$-\infty$
100	33.85	217.8	184.4	3.35	183.6	174.8	−381.9
200	39.29	242.7	207.9	6.95	181.9	166.6	−182.0
298.15	45.52	259.6	222.3	11.13	174.2	160.1	−117.4
300	45.61	259.9	222.5	11.21	174.1	160.0	−116.6
400	50.67	273.7	233.6	16.02	157.8	158.7	−86.69
500	54.56	285.5	242.8	21.30	157.0	159.0	−69.45
600	57.66	295.7	250.8	26.94	156.2	159.4	−58.07
700	60.29	304.8	257.9	32.84	155.5	160.0	−49.96
800	62.55	313.0	264.3	38.99	154.9	160.7	−43.89
900	64.60	320.5	270.1	45.35	154.4	161.4	−39.20
1000	66.44	327.4	275.5	51.88	153.9	162.3	−35.44
1100	68.07	333.8	280.5	58.62	153.6	163.1	−32.38
1200	69.54	339.8	285.2	65.52	153.2	164.0	−29.87
1300	70.88	345.4	289.6	72.51	153.0	164.9	−27.74
1400	72.01	350.7	293.8	79.66	152.7	165.8	−25.90
1500	73.05	355.7	297.8	86.94	152.5	166.7	−24.31

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (4)] (see text).

Table VIII. Ideal-Gas Thermodynamic Properties for $CHBr_2\bullet$[a]

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
(K)	$(J\cdot mol^{-1}\cdot K^{-1})$			$(kJ\cdot mol^{-1})$			
0	0.0	0.0	0.0	0.0	218.2[b]	218.2	$-\infty$
100	38.95	254.6	219.4	3.52	217.3	202.4	−442.2
200	47.66	284.2	245.0	7.82	212.0	188.3	−205.8
298.15	55.27	304.7	261.4	12.93	201.3	177.0	−129.7
300	55.40	305.1	261.7	13.01	201.2	176.9	−128.8
400	60.88	321.8	274.7	18.83	170.1	175.1	−95.69
500	64.64	335.8	285.6	25.15	169.9	176.4	−77.11
600	67.32	347.9	294.9	31.71	169.7	177.7	−64.73
700	69.37	358.4	303.3	38.58	169.6	179.0	−55.90
800	71.04	367.8	310.7	45.61	169.5	180.4	−49.29
900	72.43	376.2	317.6	52.76	169.4	181.8	−44.14
1000	73.64	383.9	323.8	60.08	169.3	183.1	−40.04
1100	74.64	391.0	329.6	67.49	169.2	184.5	−36.65
1200	75.52	397.5	335.0	75.02	169.2	185.9	−33.85
1300	76.32	403.6	340.0	82.59	169.1	187.3	−31.51
1400	76.99	409.2	344.8	90.25	169.1	188.7	−29.46
1500	77.57	414.6	349.3	97.99	169.1	190.1	−27.70

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (5)] (see text).

Table IX. Ideal-Gas Thermodynamic Properties for $CBr_3\bullet$[a]

T	C°_p	S°	$-(G^\circ - H^\circ_o)/T$	$H^\circ - H^\circ_o$	ΔH°_f	ΔG°_f	$\log K_f$
(K)	($J \cdot mol^{-1} \cdot K^{-1}$)			($kJ \cdot mol^{-1}$)			
0	0.0	0.0	0.0	0.0	253.2[b]	253.2	$-\infty$
100	50.84	273.2	233.5	3.98	252.9	233.7	−510.9
200	63.01	312.8	264.1	9.75	251.0	215.3	−235.2
298.15	69.75	339.2	284.6	16.28	231.6	198.2	−146.8
300	69.87	339.7	285.0	16.4	231.5	200.1	−145.7
400	74.14	360.4	301.3	23.64	186.0	198.9	−108.7
500	76.82	377.3	314.9	31.17	186.7	202.1	−88.32
600	78.49	391.4	326.5	38.95	187.3	205.1	−74.73
700	79.62	403.6	336.7	46.86	187.8	208.1	−64.98
800	80.37	414.3	345.7	54.85	188.3	210.9	−57.61
900	80.92	423.8	353.9	62.93	188.7	213.7	−51.88
1000	81.34	432.3	361.3	71.04	189.0	216.5	−47.32
1100	81.63	440.1	368.1	79.20	189.3	219.2	−43.56
1200	81.84	447.2	374.4	87.36	189.6	221.9	−40.42
1300	82.05	453.8	380.3	95.56	189.8	224.6	−37.78
1400	82.17	459.9	385.8	103.8	190.0	227.3	−35.48
1500	82.30	465.6	390.9	112.0	190.2	230.0	−33.51

[a] See footnote *a*, Table III.

[b] Assigned, based on isodesmic reaction [Eq. (6)] (see text).

Our theoretically estimated standard enthalpies of formation at 298 K for CH_2Br_2, $CHBr_3$, CBr_4, $CH_2Br\bullet$, $CHBr_2\bullet$, and $CBr_3\bullet$ are compared with values from several literature sources [11, 27, 29, 32–36] in Table X. These standard heats of formation have been assigned an uncertainty based on the cumulative uncertainties in the selected heats of formation of CH_4, CH_3Br, and $CH_3\bullet$. Examination of our calculated heats of formation and the literature values leads one to several conclusions. The $\Delta H^\circ_{f,298}$ for CH_2Br_2 is subject to rather high uncertainty, probably at least $\pm 8\ kJ \cdot mol^{-1}$, as no one has actually published an experimental measurement. The value of $5.85 \pm 5.0\ kJ \cdot mol^{-1}$ determined by Papina et al. [32] from their measurement of $\Delta H^\circ_{f,m}(CHBr_3, l)$, agrees closest with our computed value of $4.48\ kJ \cdot mol^{-1}$, however, it must be borne in mind that their value is only an estimate based on an additivity scheme. Our calculated value for $\Delta H^\circ_{f,298}(CHBr_3)$ of $50.88\ kJ \cdot mol^{-1}$ lends strength to the combustion calorimetry measurement of Papina et al. [32], despite the fact that Bickerton et al. [33] argued that this type of calorimetry is not suitable for tribromomethane because of decomposition of the sample. The calculated standard enthalpy of formation at 298 K for tetrabromomethane of $105.6\ kJ \cdot mol^{-1}$ once again agrees closest with the estimates by the Russian authors [32, 27], as opposed to that measured by bomb calorimetry [33].

Table X. Comparison of Computed and Experimental Heats of Formation at 298 K[a]

Species	$\Delta H^{\circ}_{f,298}$(calc.)[b]	$\Delta H^{\circ}_{f,298}$(lit.)	Ref. No.
CH_2Br_2	4.48 ± 0.5	5.86 ± 5.02	32
		10.0 ± 15.0	27
		−14.77 ± 3.4	11
$CHBr_3$	50.88 ± 0.5	55.23 ± 3.4	32
		60.0 ± 15.0	27
		23.85 ± 4.6	29
		16.74 ± 3.4	11
CBr_4	105.6 ± 0.5	83.89 ± 3.4	33
		115.9 ± 3.9	32
		120.0 ± 15.0	27
		79.5 ± 4.2	11
$CH_2Br\bullet$	174.2 ± 0.7	173.6	34
		169.0 ± 4.2	35
		168.2	36
$CHBr_2\bullet$	201.3 ± 0.7	227.2	34
		188.3 ± 8.4	35
		185.8	36
$CBr_3\bullet$	231.6 ± 0.7	235.0 ± 25.0	27
		205.0	36

[a] Values in $kJ \cdot mol^{-1}$.

[b] Assigned uncertainties based on the cumulative experimental uncertainties in CH_4, CH_3Br, and $CH_3\bullet$.

The theoretical $\Delta H^{\circ}_{f,298}$'s for the radicals $CH_2Br\bullet$ and $CHBr_2\bullet$ agree very well with our previous critical examination of thermochemical and kinetic data on the bromination of halomethanes [35]. The more recent measurement of the heats of formation of all three bromomethyl radicals by monoenergetic electron impact [36], while agreeing quite well with our computed values for the mono- and dibromo radicals, differs quite substantially for $CBr_3\bullet$, probably because of the adoption of the old and now untenable $\Delta H^{\circ}_{f,298}(CHBr_3) = 23.8\ kJ \cdot mol^{-1}$.

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