Thermodynamic Properties of Bromomethanes and Bromo-methyl Radicals: An *ab initio* Study[1]

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ABSTRACT

Thermochemical data on volatile organic compounds containing bromine is 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 using the GAUSSIAN 92 system of programs. 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. This data was then used in the determination of $\Delta H^o_{f,T}$, $\Delta G^o_{f,T}$, and $K_{f,T}$ for all species over the temperature range 0–1500 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

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 is 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 being 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 ($CH_{3-m}Br_m$ 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, but 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]. 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 the 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 anharmonic 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 MP4/6-31G** levels based on MP2/6-31G* optimized structures; energies at the higher electron correlation level being approximately 0.05 Hartrees lower. The MP4/6-31G** single point energies along with the ZPEs were used to compute the reaction enthalpies for the following isodesmic reactions:

$$2CH_3Br \text{ fi } CH_2Br_2 + CH_4 \qquad (1)$$

$$3CH_3Br \text{ fi } CHBr_3 + 2CH_4 \qquad (2)$$

$$4CH_3Br \text{ fi } CBr_4 + 3CH_4 \qquad (3)$$

$$CH_3Br + CH_3\bullet \rightarrow CH_2Br\bullet + CH_4 \quad (4)$$

$$CH_2Br_2 + CH_3\bullet \rightarrow CHBr_2\bullet + CH_4 \quad (5)$$

$$CHBr_3 + CH_3\bullet \rightarrow CBr_3\bullet + CH_4 \quad (6)$$

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 0K ($\Delta H^o_{f,0}$) for methyl bromide to be -5.15 kcal/mol based on an arithmetic average of the selected values appearing in the following four standard compendia: (a) Kudchadker and Kudchadker [11],-5.34; (b) Gurvich *et al* [27], -5.02; (c) Wagman *et al* [28], -4.74; and (d) Lias *et* [29], -5.5 kcal/mol. The standard enthalpy of formation for methane at 0K was calculated from spectroscopic data [25] to be -15.99±0.08 from the tabulated value at 298K of -17.895±0.08 in the JANAF thermochemical tables [30]. From these two selected heats of formation along with calculated theoretical reaction enthalpies ($\Delta H^o_0(Rx)$), the standard enthalpy of formation at 0K 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 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 $\Delta H^o_{f,0}(CH_3\bullet)$ to be 35.71±0.01 kcal/mol from $\Delta H^o_{f,298}(CH_3\bullet)$ = 35.1±0.1 kcal/mol as measured by Heneghan, Knoot, and Benson [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.

Ideal gas thermodynamic functions C^o_p, S^o, $-(G^o-H^o_o)/T$, and $H^o-H^o_o$ in the temperature range 0–1500K and 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 for the radicals. The results are listed in Tables III–IX.

Our theoretically estimated standard enthalpies of formation at 298 K for CH_2Br_2, $CHBr_3$, CBr_4, CH_2Br•, $CHBr_2$•, and CBr_3• are compared with values from several literature sources [11,27,29,32–36] in Table X. Examination of our calculated heats of formation and the literature values leads one to several conclusions. The $\Delta H^o_{f,298}$ for CH_2Br_2 is subject to rather high uncertainty, probably at least ±2 kcal/mol, as no one has actually published an experimental measurement. The value of 1.4±1.2 kcal/mol determined by Papina *et al* [32] from their measurement of $\Delta H^o_{f,m}(CHBr_3,l)$, agrees closest with our computed value of 1.07 kcal/mol, however it must be borne in mind that their value is only an estimate based on an additive scheme. Our calculated value for $\Delta H^o_{f,298}(CHBr_3)$ of 12.16 kcal/mol 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 48.11 kcal/mol once again agrees closest with the estimates by the Russian authors [32,27] as opposed to that measured by bomb calorimetry [33]. The theoretical $\Delta H^o_{f,298}$'s for the radicals CH_2Br• and $CHBr_2$•, 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 di-bromo radicals, differs quite substantially for CBr_3•, probably because of the adoption of the old and now untenable $\Delta H^o_{f,298}(CHBr_3)$ = 5.7 kcal/mol.

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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*)
CH_4	-40.33255	-40.38864	30.0
CH_3Br	-2610.00866	-2610.06460	25.1
CH_2Br_2	-5179.68265	-5179.73838	19.2
$CHBr_3$	-7749.35392	-7749.40944	12.4
CBr_4	-10319.02126	-10319.07690	5.0
CH_3•	-39.66875	-39.71475	19.4
CH_2Br•	-2609.34887	-2609.39548	15.2
$CHBr_2$•	-5179.02863	-5179.07545	9.9
CBr_3•	-7748.70664	-7748.75350	3.7

[a]Total energies in Hartrees.

[b]Unscaled zero-point vibrational energies in kcal/mol.

Table II. Theoretical Reaction Energies, ΔE; Zero-Point Energy Corrections, $\Delta(ZPE)$; Reaction Enthalpies, $\Delta H^o_0(Rx)$; and Heats of Formation, $\Delta H^o_{f,0}$, at 0K[a].

Species	Isodesmic Reaction #[b]	ΔE[c]	$\Delta(ZPE)$[d]	$\Delta H^o_0(Rx)$[e]	$\Delta H^o_{f,0}$[f]
CH_2Br_2	1	1.37	-0.89	0.89	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_2Br•	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 in kcal/mol.
[b]See isodesmic reaction # in the text.
[c]Evaluated at the MP4/6-31G**//MP2/6-31G* level.
[d]Scaled by 0.8929.
[e]$\Delta H^o_0(Rx) = \Delta E + \Delta(ZPE)$.
[f]From computed $\Delta H^o_0(Rx)$ and known heats of formation of other species in the isodesmic reactions.

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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^o_p, $-(G^o-H^o_o)/T$, and $H^o-H^o_o$ 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^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

T	C^o_p	S^o	$-(G^o-H^o_o)/T$	$H^o-H^o_o$	ΔH^o_f	ΔG^o_f	$\log K_f$
K	cal $K^{-1}mol^{-1}$			kcal mol^{-1}			
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 III.

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

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

Species	$\Delta H^o_{f,298}$(calc.)	$\Delta H^o_{f,298}$(lit.)	Ref.
CH_2Br_2	1.07	1.4±1.2	32
		2.39±3.59	27
		-3.53±0.8	11
$CHBr_3$	12.16	13.2±0.8	32
		14.34±3.59	27
		5.7±1.1	29
		4.0±0.8	11
CBr_4	25.23	20.05±0.81	33
		27.7±0.93	32
		28.68±3.59	27
		19.0±1.0	11
CH_2Br•	41.63	41.5	34
		40.4±1	35
		40.2	36
$CHBr_2$•	48.11	54.3	34
		45.0±2	35
		44.4	36
CBr_3•	55.36	56.17±5.98	27
		49.0	36

[a] Values in kcal/mol.