J. Phys. Chem. A **2008,** *112,* 4951–4957

Theoretical Studies on the Thermochemistry of Stable Closed-Shell C1 and C2 Brominated Hydrocarbons

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Received: September 16, 2007; Revised Manuscript Received: March 10, 2008

The enthalpies of formation of stable closed shell C1 and C2 brominated hydrocarbons have been predicted using Gaussian-3X model chemistry. The entropy, heat capacity, and thermal corrections are calculated from B3LYP/6-31G(2df,p) geometries and vibrational frequencies using rigid-rotor−harmonic-oscillator approximation, except for the quantities of the internal rotations in ethanes, which are calculated using the quantum-mechanical energy levels. Enthalpies of formation have been obtained from G3X atomization and isodesmic reactions. Good agreement is observed on the well-established experimental enthalpies of formation of CH_3Br, CH_2Br_2, CH_2ClBr, and C_2H_3Br from the high-resolution threshold photoelectron photoionization coincidence study.

I. Introduction

The chemistry of brominated hydrocarbons is important in a variety of areas including combustion, fire suppression, and atmospheric chemistry in both stratosphere and troposphere. Bromomethane, man-made Halons, and a group of short-lived, naturally occurring species (CH_2Br_2, $CHBr_3$, CH_2ClBr, $CHBrCl_2$, $CHBr_2Cl$, etc.) are their main constituents in the atmosphere,[1] of which Halon is or will be phased out as part of the Montreal Protocol. In the atmosphere, their removal, besides deposition, is initialized by photodissociation and/or H-abstraction by OH radical; while in flame, where they serve as flame retardant, the reactions are fairly complicated, and the kinetics study has been hampered by the lack of precise and accurate thermodynamic data. For example, the measured and predicted enthalpies of formation are rather diverse for CH_2Br_2 (-12.5 ± 8.3,[2] -14.8 ± 3.3,[3] -11.1 ± 5.0,[4] 5.9 ± 1.7,[5] 4.8 ± 4.2,[6] 3.6 ± 3.4[7]), $CHBr_3$ (16.7 ± 3.9,[3] 23.8 ± 4.5,[4] 79,[2] 55.3 ± 3.3,[5] 60 ± 15,[8] 50.9,[6] 51.6,[9] 54.3 kJ/mol[10]), and CBr_4 (79.5 ± 3.4,[3] 83.9 ± 3.4,[4] 116.0 ± 3.9,[5] 105.6,[6] 110.6,[9] 118.1 kJ/mol[10]), and the information for many of the brominated ethylenes, ethanes and free radicals is completely missing. Systematic evaluations have been done on the fluorinated and chlorinated hydrocarbons.[11,12]

The experimental determination of the enthalpies of formation of bromocompounds has used methods including calorimetry,[4,5] chemical equilibrium,[13] and, recently, high-resolution dissociative photoionization, such as threshold photoelectron photoionization coincidence (TPEPICO) studies,[7,14,15] and so forth. The combustion study has difficulty in determining the final state of bromine products, while the equilibrium study can yield only the relative energetics. Alternatively, theoretical methods at different correlation levels[6,9,10,16,17] and empirical bond-additivity methods[2,3,18] have been used extensively to predict the structural and thermodynamic properties of these compounds. The theoretical calculations have revealed significant discrepancies to the experimental measurements and bond-additivity predictions.[9,10] In the present study, the thermodynamic properties of closed-shell C1 and C2 brominated hydrocarbons have been predicted theoretically at a medium correlation level of Gaussian-3X (G3X).[19,20]

II. Computational Methods

All density functional theory (DFT) and molecular orbital theory calculations are carried out using the Gaussian 03 suite of programs.[21] The equilibrium structures are first optimized by the DFT method using Becke's three parameter hybrid functional together with the LYP correlation functional (B3LYP[22]) with a basis set of 6-31G(2df,p).[23] The B3LYP/6-31G(2df,p) vibrational frequencies are used for the evaluation of the zero-point energy (ZPE) corrections with a scale factor of 0.9854,[19] and the geometries for moments of inertia. The geometries are further optimized at the B3LYP level with a larger basis set of 6-311+G(3df,2p)[24] before being submitted for single point electronic energies using G3X model chemistry,[19,20] which approximates a correlation level of QCISD(T,Full)/G3ExtraLarge. Spin−orbital interactions are added to atomic species only,[25] while no further relativistic effects are included. Benchmark calculations have shown that G3X standard deviation to the experimental results is not improved with the inclusion of nonscalar relativistic effects.[26] The G3X procedure here differs from the original one only on the molecular geometry used for electronic energy calculation.

The B3LYP vibrational frequencies and geometries are employed for the evaluation of entropies, heat capacities, and thermal corrections using the rigid-rotor−harmonic-oscillator (RRHO) approximation, except for the torsion motion in bormoethanes, which are treated here quantum mechanically by numerically solving the Schrödinger equation using the Fourier grid Hamiltonian (FGH) method.[27] The obtained energy levels are used to calculate the partition function and the thermodynamic parameters. The torsion potential energy curves are fitted by truncated cosine functions as

$$2V(\varphi) = V_0 + V_1 \cos(\varphi) + V_2 \cos(2\varphi) + V_3 \cos(3\varphi) + V_4 \cos(4\varphi) + V_6 \cos(6\varphi) + V_{12} \cos(12\varphi) \quad (1)$$

where ϕ is the torsion angle. G3X energies as functions of torsion angles are calculated by scanning the torsion angles at

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10.1021/jp0774443 CCC: $40.75

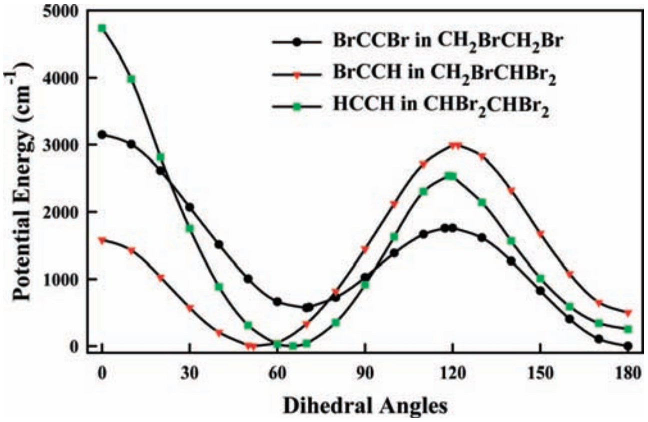

Figure 1. Potential energy curves for internal rotations about the C−C bonds of CH_2BrCH_2Br, $CH_2BrCHBr_2$, and $CHBr_2CHBr_2$ at the G3X level.

10° intervals and allowing the remaining geometrical parameters to be optimized at the B3LYP/6-31G(2df,p) and B3LYP/6-311+G(3df,2p) levels, with ZPE corrections at the B3LYP/6-31G(2df,p) level. Figure 1 shows the potential energy curves for internal rotations of CH_2BrCH_2Br, $CH_2BrCHBr_2$, and $CHBr_2CHBr_2$, while, for other bromoethanes, they are approximated to include V_0 and V_3 terms only. The moment of inertia is computed about the axis passing through the centers-of-mass of both the rotating methyl groups.[28] The first 160 torsion energy levels are evaluated and utilized for calculation of the thermodynamic contribution of the torsion modes. The molecular parameters used in thermodynamic function calculations, including the molecular symmetry, the rotational moment of inertia, the harmonic vibrational frequencies, and the reduced moment of inertia and potential energy parameter for the torsion motions in brominated ethanes are given as Supporting Information (Tables S1 and S2). The ZPEs, G3X electronic and atomization energies, and the thermal corrections at 298 K ($H^T - H^0$) are also listed in Table S3.

III. Results and Discussion

The thermodynamic properties of brominated compounds have not been investigated as intensively as their chlorinated and fluorinated counterparts. Traditional calorimetry has difficulty in determining the final state of bromine products, while theoretical study suffers from the high demand on computational resources and the sophisticated model for relativistic effects. Here the G3X theory is employed to predict the enthalpies of formation of brominated closed-shell C1 and C2 hydrocarbons, and the results are summarized in Tables 1 and 2.

A. Bromomethanes. There have been several experimental and theoretical determinations on $\Delta_f H^\circ(CH_3Br)$. Three experimental measurements[15,29,30] yield consistent $\Delta_f H^\circ_{298K}$ in the range of −36.7 to −38.0 kJ/mol, while the value −34.3 ± 0.8 kJ/mol from the chemical equilibrium study of $CH_4 + Br_2 \rightarrow CH_3Br + HBr$ is higher than other values by ca. 3 kJ/mol.[31] The lower values are supported by theoretical calculations of −37.2 ± 3.3 kJ/mol at the G2 level with isodesmic or hydrogenation reactions,[32] of −37.6 kJ/mol at the CCSD(T) level extrapolated to the infinite basis limit with atomization reaction,[33] and of −36.9 kJ/mol from G3X atomization energy in the present study. The well-established $\Delta_f H^\circ_{0K} = -21.30 \pm 0.42$ kJ/mol ($\Delta_f H^\circ_{298K} = -36.7$ kJ/mol) from the TPEPICO study of CH_3Br[15] will be used for the calculation of the enthalpies of other bromocompounds using the following isodesmic reactions:

$$C_nH_{M-x}Br_x + xCH_4 \rightarrow C_nH_M + xCH_3Br \qquad (R1)$$

where $n = 1$ and $M = 4$ for methanes, and $n = 2$ and $M = 2$, 4, and 6 for acetylenes, ethylenes, and ethanes, respectively. The corrections using these isodesmic reactions are small because of the excellent agreement between the experimental values and theoretical values from G3X atomization reactions for the enthalpies of formation of CH_4, C_2H_n ($n = 2, 4, 6$), and CH_3Br.

The $\Delta_f H^\circ(CH_2Br_2)$ from several empirical schemes spans a range of ∼20 kJ/mol. $\Delta_f H^\circ_{298K} = -12.5 \pm 8.3$ kJ/mol was first estimated from the interactions between atoms or bonds.[2] A similar value of −14.8 ± 3.3 kJ/mol was obtained by the Kudchadkers using the group additivity method,[3] and a value of −11.1 ± 5.0 kJ/mol was obtained by Bickerton et al.[4] using the Allen bond-energy scheme according to the experimental values of CH_4, CH_3Br, and CBr_4. A value of 5.9 ± 1.7 kJ/mol has also been estimated by Papina et al.[5] by interpolating data for CH_3Br and $CHBr_3$, which are, however, in great suspicion. The only experimental determination was performed recently by Lago et al.[7] from the dissociative photoionization of CH_2Br_2, CH_2ClBr, and CH_2Cl_2. From the measured appearance energies (AEs) of CH_2Cl^+ and CH_2Br^+ ions and the well-established $\Delta_f H^\circ_{298K}(CH_2Cl_2) = -95.1 \pm 2.5$ kJ/mol (−88.3 kJ/mol at 0 K),[12] $\Delta_f H^\circ_{0K} = 24.9$ and $\Delta_f H^\circ_{298K} = 3.6 \pm 3.4$ kJ/mol are derived for CH_2Br_2. Theoretical predictions have unexceptionally supported the higher values by Papina et al. and Lago et al. Using the isodesmic reaction R1, $\Delta_f H^\circ_{298K}(CH_2Br_2) = 4.5$ kJ/mol at the MP4/6-31G**//MP2/6-31G* level,[6] 4.8 kJ/mol at the DK-CCSD(T)//Aug-VTZ level,[10] 4.3 kJ/mol at the QCISD(T)/6−311+G(3df,2p)//QCISD/6−311G(d,p) level,[9] and 1.4 and 1.3 kJ/mol using G3X atomization energy and isodesmic reaction R1 here. All the theoretical values agree within the experimental uncertainty of Lago et al. Note that $\Delta_f H^\circ_{0K}(CH_2ClBr) = -29.6 \pm 1.9$ kJ/mol from Lago et al. and $D_0(CH_2Cl{-}Br) = 266.3 \pm 1.0$ kJ/mol by Li et al.[34] are also supported by our G3X predictions of −31.1 and 266.6 kJ/mol.

The available data for $\Delta_f H^\circ(CHBr_3)$ are rather diverse. At the lower end are the group additivity prediction of 16.7 ± 3.9 kJ/mol by the Kudchadkers[3] and the interpolation of 23.8 ± 4.5 kJ/mol from values of CH_4, CH_3Br, and CBr_4 by Bickerton et al.[4] At the high end are the bond interaction prediction of 79 kJ/mol by Berntein[2] and the combustion study of 55.3 ± 3.3 kJ/mol by Papina et al.[5] Gurvich et al. cited 60 ± 15 kJ/mol,[8] preferring the combustion result. Using isodesmic reaction R1, theoretical studies have also predicted $\Delta_f H^\circ_{298K} = 50.9$ kJ/mol at the MP4/6-31G**//MP2/6-31G* level,[6] and 51.6 kJ/mol at the QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) level.[9] Using another isodesmic reaction $CH_3Br + CHBr_3 \rightarrow 2CH_2Br_2$, Oren et al. obtained a value of 54.3 kJ/mol, even though the experimental value used for CH_2Br_2 is not clearly mentioned.[10] G3X results are 43.9, 43.5, and 48.1 kJ/mol using the atomization and these two isodesmic reactions, respectively. A G3X value of 45.8 kJ/mol can also be obtained using isodesmic reaction $CH_3Br + CH_2Br_2 \rightarrow CH_4 + CHBr_3$. All the theoretical studies agree within 8 kJ/mol and suggest moderate reliability of the combustion result by Papina et al.

For $\Delta_f H^\circ_{298K}(CBr_4)$, on the low end are the group additivity prediction of 79.5 ± 3.4 kJ/mol[3] and the calorimetric study of 83.9 ± 3.4 kJ/mol,[4] and on the high end is the extrapolation of 116.0 ± 3.9 kJ/mol by Papina et al. from the enthalpies of formation of CH_3Br and $CHBr_3$.[5] Theoretical studies using isodesmic reaction R1 have obtained $\Delta_f H^\circ_{298K} = 105.6$ kJ/mol at the MP4/6-31G**//MP2/6-31G* level,[6] 110.6 kJ/mol at the QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) level,[9] and

TABLE 1: The Predicted Enthalpies of Formation at the G3X Level (in kJ/mol)

	G3X[a]				others		
	0 K	298 K					
	AR	AR	R1	R′	empirical	theoretical	experimental[c]
CH_4	−67.1	−75.1					**−74.6 ± 0.3**12
CH_3Br	−21.5	−36.9				−33.9[c]	**−36.7 ± 0.42**,[15] −37.5 ± 1.5,[30] −38.0 ± 1.3[29] −34.3 ± 0.8,[31] −37.2 ± 3.3,[32] −37.6[33]
CH_2Br_2	22.7	1.4	1.3		−12.5 ± 8.3[d] −14.8 ± 3.3[f] −11.1 ± 5.0[l]	9.1,[c] 4.8[e] 4.3,[g] 4.5[h]	**3.6 ± 3.4**,[7] 5.9 ± 1.7,[5] 4.8 ± 4.3[9]
$CHBr_3$	69.8	43.9	43.5	48.1[j]	79[d] 16.7 ± 3.9[f]	58.9,[c] 54.3[e] 51.6,[g] 50.9[h]	23.8 ± 4.5,[4] 79,[2] 55.3 ± 3.3,[5] 60 ± 15[8]
CBr_4	125.4	96.0	95.3	100.1[k]	79.5 ± 3.4[f]	119.3,[c] 118.1[e] 110.6,[g] 105.6[h]	83.9 ± 3.4,[4] 116.0 ± 3.9,[5]
HCCH	228.8	228.3					**227.4 ± 0.8**[12]
HCCBr	280.6	274.0	272.8			285.6,[c] 280.1[e]	262 ± 6[35]
BrCCBr	330.0	318.8	317.3			334.6,[c] 335.3[e]	
C_2H_4	60.4	51.8					**52.4 ± 0.5**[12]
CH_2CHBr	86.6	71.7	72.0			79.6,[l] 70.1[m]	**74.1 ± 3.1**,[38] 79.2 ± 3.1[36,37]
CH_2CBr_2	121.1	100.9	100.9	105.1[n]			
Z-CHBrCHBr	117.2	96.8	96.8	101.0[n]			
E-CHBrCHBr	117.5	97.9	97.9	102.1[n]			
$CHBrCBr_2$	153.4	128.7	128.4	134.7[n]		147.2,[c] 144.2[e]	
C_2Br_4	193.9	165.4	164.8	173.2[n]		191.6,[c] 190.1[e]	
C_2H_6	−68.4	−84.0					**−84.0 ± 0.4**[12]
CH_3CH_2Br	−43.2	−65.0	−65.3		−66.1 ± 0.9[f]		−63.6 ± 2.1,[37] −64.6 ± 2.1[51] −61.9 ± 1.0,[30] −65.3 ± 6.3[52]
CH_3CHBr_2	−11.0	−38.2	−38.8		−41.0 ± 4.6[f]		−32.2[53]
CH_2BrCH_2Br	−16.5	−42.5	−43.8				−42.2[53]
CH_3CBr_3	31.3	0.0	−0.9		−4.6 ± 7.5[f]		
$CH_2BrCHBr_2$	21.8	−9.8	−10.9				
CH_2BrCBr_3	67.9	32.1	30.9		33.1 ± 7.5[f]		
$CHBr_2CHBr_2$	63.0	27.2	25.5				
$CHBr_2CBr_3$	112.5	72.7	71.2		79.5 ± 10.5[f]	113.1[e]	
C_2Br_6	166.1	122.8	121.0		133.1 ± 15.1[f]	170.3,[c] 165.5[e]	
H	216.0	218.0					
C	711.9	716.7					
Br	117.9	111.9					

[a] Methods used for obtaining the enthalpies of formation: AR = G3X atomization energy, R1 = G3X with isodesmic reaction R1; [b] Experimental values from the literature; see text for details. The **bold** values are used as references in the isodesmic reaction scheme. [c] G2 predictions using isodesmic reaction R1 (ref 10). [d] Bond interaction estimations (ref 2). [e] DK-CCSD(T)/Aug-VTZ predictions using isodesmic reaction R1 (ref 10). [f] Group additivity estimations (ref 3). [g] QCISD(T)/6-311+G(3df,2p)-ECP predictions using isodesmic reaction R1 (ref 9). [h] MP4/6-311G** predictions using R1 (ref 6); [l] Bond energy scheme estimation (ref 4). [j] From isodesmic reaction $CH_3Br + CHBr_3 \rightarrow 2\,CH_2Br_2$ at the G3X level. [k] From isodesmic reaction $CH_4 + CBr_4 \rightarrow 2\,CH_2Br_2$ at the G3X level. [l] G2(ECP) prediction with R1 (ref 16); [m] G2 prediction (ref 38); [n] From isodesmic reaction R2 at the G3X level.

118.1 kJ/mol at the DK-CCSD(T)/Aug-VTZ level.[10] The results from G3X atomization and isodesmic reaction R1 are 96.0 and 95.3 kJ/mol, respectively. A G3X value of 100.1 kJ/mol can also be obtained from isodesmic reaction $CH_4 + CBr_4 \rightarrow 2CH_2Br_2$.

$\Delta_f H^{\circ}_{298K}(CBr_4) - \Delta_f H^{\circ}_{298K}(CHBr_3) = 60.2 \pm 3.0$ kJ/mol has been determined from the equilibrium constant study of $CHBr_3 + Br_2 \rightarrow CBr_4 + HBr$ by King et al., assuming no other product channels from $CHBr_3 + Br_2$.[13] The G3X difference is 51.8 kJ/mol. Nevertheless, the measurement was based on the equilibrium constants within a rather narrow temperature range of 587−590 K, even though previous theoretical studies have predicted the differences as 54.7 kJ/mol at the MP4/6-31G** level,[6] 59.0 kJ/mol at the QCISD(T)/6-311+G(3df,2p) level,[9] and 63.8 kJ/mol at the DK-CCSD(T)/Aug-VTZ level.[10]

B. Bromoacetylenes. Okabe has obtained $\Delta_f H^{\circ}_{0K}(HCCBr) = 269 \pm 6$ kJ/mol and $\Delta_f H^{\circ}_{298K} = 262 \pm 6$ kJ/mol from the difference in the AEs of electronically excited HCC radical in the VUV photodissociation of HCCH and HCCBr.[35] The value is lower than our G3X predictions of 274.0 and 272.8 kJ/mol (at 298 K) using atomization and the isodesmic R1 reaction, and even lower than Oren et al.'s predictions of 280.1 kJ/mol using isodesmic reaction R1 at the DK-CCSD(T)/Aug-VTZ level and 282.4 kJ/mol at the W2DK level.[10]

There is no experimental measurement on the enthalpy of formation for dibromoacetylene. Oren et al. predicted $\Delta_f H^{\circ}_{298K}(C_2Br_2) = 333.6$ kJ/mol using isodesmic reaction R1 at the DK-CCSD(T)/Aug-VTZ level,[10] being higher again than our G3X prediction of 317.3 kJ/mol using the same isodesmic reaction.

C. Bromoethylenes. The experimental measurement on the enthalpies of formation of bromoethylenes is available to C_2H_3Br only. From the measured heat of hydrogenation $\Delta_r H^{\circ}_{298K} = -199.2 \pm 1.9$ kJ/mol for reaction $C_2H_3Br + 2H_2 \rightarrow C_2H_6 + HBr$, Lacher et al. obtained $\Delta_f H^{\circ}_{298K}(C_2H_3Br) = 78.2 \pm 1.9$ kJ/mol,[36] and Cox and Pilcher later adjusted it to 79.2 ± 1.9 kJ/mol.[37] The value has received support from theoretical G2(ECP) calculation, which predicted a value of 79.6 kJ/mol using isodesmic reaction $C_2H_3Br + CH_4 \rightarrow C_2H_4 + CH_3Br$.[16] These values are ∼5 kJ/mol higher than those of the recent study by Lago and Baer[38] who obtained $\Delta_f H^{\circ}_{0K} = 89.1$ and $\Delta_f H^{\circ}_{298K} = 74.1 \pm 3.1$ kJ/mol from TPEPICO $AE(C_2H_3^+)$ in $C_2H_3Br + h\nu \rightarrow C_2H_3^+ + Br + e$ and a W2 prediction of $\Delta_f H^{\circ}_{0K}(C_2H_3^+) = 1119.6$ kJ/mol, where the $AE(C_2H_3^+)$ is consistent with an early

TABLE 2: The Calculated Entropies (S, in J K^{-1} mol^{-1}), Heat Capacities (C_P, in J K^{-1} mol^{-1}), and Thermal Corrections ($H^T - H^0$, in kJ mol^{-1}) of Bromoethanes at Different Tempaeratures (in Kelvin)

		298.15	400	500	600	800	1000	1200	1500
CH_3CH_3	S	229.56	246.73	262.56	277.63	305.66	331.11	354.27	385.26
	S_{Calc}[a]	229.01	245.91	261.63	276.41	304.15	329.40	352.41	383.25
	S_{Expt}[b]	229.16	246.38	262.34	277.57	305.90	331.63	355.01	386.26
	C_P	52.54	65.05	77.20	88.24	106.75	121.29	132.59	144.89
	$C_{P,\text{ Calc}}$[a]	51.73	64.08	76.19	87.23	105.81	120.44	131.83	144.23
	$C_{P,\text{ Expt}}$[b]	52.49	65.46	77.94	89.19	107.94	122.55	133.80	145.90
	$H^T - H^0$	11.96	17.94	25.06	33.35	52.92	74.78	101.22	142.96
CH_3CH_2Br	S	288.02	309.03	328.02	345.65	377.34	405.15	429.87	462.33
	S_{KK}[c]	287.27	308.24	327.27	345.01	376.98	405.05	429.95	462.67
	C_P	64.59	78.93	91.43	101.92	118.38	130.76	140.22	150.44
	$C_{P,\text{KK}}$[c]	64.22	79.04	91.92	102.68	119.45	131.92	141.38	151.46
	$H^T - H^0$	13.69	21.01	29.54	39.24	61.34	86.31	113.45	157.15
	$H^T - H^0$[c]	13.56	20.88	29.46	39.20	61.46	86.69	114.06	158.07
CH_3CHBr_2	S	327.95	353.55	375.99	396.31	431.83	462.11	488.49	522.53
	S_{KK}[c]	327.48	352.96	375.35	395.64	431.16	461.54	487.98	522.12
	C_P	80.07	94.59	106.57	116.22	130.54	140.77	148.39	156.50
	$C_{P,\text{KK}}$[c]	79.58	94.22	106.36	116.15	130.71	141.13	148.82	156.98
	$H^T - H^0$	16.42	25.33	35.41	46.57	71.33	98.51	127.47	173.28
	$H^T - H^0$[c]	16.32	25.19	35.23	46.36	71.17	98.41	127.40	173.38
CH_2BrCH_2Br	S	333.03	359.80	383.07	403.95	440.11	470.72	497.27	531.45
	C_P	83.79	98.58	110.00	118.96	132.28	141.94	149.20	156.87
	$H^T - H^0$	17.60	26.91	37.36	48.53	74.03	101.50	130.65	176.64
CH_3CBr_3	S	357.09	388.16	414.43	437.59	477.05	509.86	537.93	573.61
	S_{KK}[c]	354.13	384.80	410.87	433.96	473.38	506.26	534.42	570.20
	C_P	99.20	112.47	122.91	131.13	142.94	150.99	156.79	162.81
	$C_{P,\text{KK}}$[c]	97.74	111.42	122.21	130.79	143.09	151.42	157.32	163.34
	$H^T - H^0$	20.33	31.13	42.92	55.64	83.13	112.57	143.38	191.38
	$H^T - H^0$[c]	19.92	30.59	42.30	54.98	82.42	111.92	142.84	191.00
$CH_2BrCHBr_2$	S	379.948	409.962	435.678	458.5	497.454	529.809	557.428	592.465
	C_P	94.902	109.569	120.836	129.375	140.773	148.721	154.127	159.701
	$H^T - H^0$	20.001	30.439	41.986	54.515	81.653	110.68	140.994	188.129
CH_2BrCBr_3	S	406.98	442.03	471.26	496.70	539.31	574.05	603.30	639.92
	C_P	112.62	126.01	135.84	143.11	152.69	158.47	162.24	165.86
	$H^T - H^0$	23.85	36.04	49.16	63.12	92.79	123.95	156.04	205.30
$CHBr_2CHBr_2$	S	413.70	448.09	476.72	501.59	543.09	576.92	605.46	641.34
	C_P	110.45	123.57	132.92	139.66	148.60	154.42	158.58	162.92
	$H^T - H^0$	23.81	35.76	48.61	62.25	91.15	121.49	152.81	201.08
	$H^T - H^0$[d]	22.42	34.16	46.94	60.68				
$CHBr_2CBr_3$	S	443.48	483.50	516.22	544.19	590.06	626.69	657.11	694.79
	S_{Calc}[e]	439.19					626.14		
	C_P	129.82	142.37	150.59	156.06	162.38	165.76	167.85	169.82
	$C_{P,\text{ Calc}}$[e]	126.61	138.78	147.15	153.18	161.00	165.98	169.28	172.38
	$H^T - H^0$	27.81	41.71	56.39	71.74	103.65	136.50	169.87	220.55
C_2Br_6	S	462.74	508.62	545.37	576.30	626.18	665.33	697.44	736.74
	S_{KK}[c]	459.57	503.92	539.61	569.74	618.65	657.39	689.44	729.02
	S_{Calc}[e]	459.11					657.89		
	C_P	150.42	161.38	167.70	171.42	174.86	175.93	176.16	176.03
	$C_{P,\text{ KK}}$[c]	145.35	156.36	163.05	167.36	172.30	174.89	176.48	177.95
	$C_{P,\text{ Calc}}$[e]	146.65	157.44	163.93	168.03	172.67	175.14	176.65	178.03
	$H^T - H^0$	32.28	48.21	64.69	81.67	116.36	151.46	186.67	239.51
	$H^T - H^0$[c]	31.46	46.90	62.89	79.41	113.47	148.20	183.34	236.52

[a] From summation over the numerically evaluated energy levels based, by Vansteenkiste et al. (ref 49). [b] From Gurvich et al. (ref 8). [c] Estimated by Kudchadker and Kudchadker (ref 18). [d] Calculations by Butler et al. (ref 56). [e] Calculations by Oren et al. (ref 10).

TPEPICO measurement.[14] $\Delta_f H^{\circ}_{0K} = 88.2$ kJ/mol has also been predicted from a series of quantum mechanical calculations using the isodesmic reaction.[38] The values by Lago and Baer are supported by the present G3X predictions of $\Delta_f H^{\circ}_{0K} = 86.6$ kJ/mol and $\Delta_f H^{\circ}_{298K} = 71.7$ kJ/mol obtained from atomization energies, and $\Delta_f H^{\circ}_{298K} = 72.0$ kJ/mol from the isodesmic reaction R1, all being within the experimental uncertainty range.

For *E*- and *Z*-1,2-$C_2H_2Br_2$, two equilibrium studies have obtained an energy difference of less than 1 kJ/mol, even though they are contradictory in the lowest form.[39] The present G3X calculation shows that the enthalpy difference is only 0.2 kJ/mol at 0 K and 1.1 kJ/mol at 298 K with the *Z*-conformer being marginally lower. Isomer 1,2-$C_2H_2Br_2$ is slightly less stable by 4 kJ/mol than *Z*-CHBr=CHBr.

Since the G3X enthalpies of formation of CH_4, C_2H_4, and CH_3Br using atomization reactions are in excellent agreement with the experimental values, the improvements with isodesmic reaction R1 are small. For C_2HBr_3, the G3X values of $\Delta_f H^{\circ}_{298K}$ are 128.7 and 128.4 kJ/mol using atomization and isodesmic reaction R1, respectively, and for C_2Br_4 the values are 165.4 and 164.8 kJ/mol.

Besides R1, it seems more proper to employ the following isodesmic reaction R2 for bormoethylenes with all Br atoms attached to C=C double bonds, recognizing the recently established $\Delta_f H^\circ_{298K}(CH_2CHBr) = 74.1 \pm 3.1$ kJ/mol,[38] even though the propagation of uncertainty is fairly large:

$$C_2H_{4-x}Br_x + (x-1)C_2H_4 \rightarrow xC_2H_3Br \qquad (R2)$$

The derived $\Delta_f H^\circ_{298K}$ for CH_2CBr_2, *Z*-CHBrCHBr, *E*-CHBrCHBr, C_2HBr_3, and C_2Br_4 are 105.1, 101.0, 102.1, 133.7, and 173.2 kJ/mol, respectively, being higher than the ones obtained from R1 by ca. 2 kJ/mol per bromine substitution. The G3X results for C_2HBr_3 and C_2Br_4 using both isodesmic reactions are much lower than the values of 144.2 and 190.1 kJ/mol obtained at the DK-CCSD(T)/Aug-VTZ level using reaction R1.[10]

D. Rotameric Stability, Internal Rotation Barriers, and Thermodynamic Properties of Bromoethanes. The internal rotations in bromoethanes are hindered by barriers. The G3X barrier heights for torsion motion in C_2H_5Br, CH_3CHBr_2, CH_3CBr_3, CH_2BrCBr_3, C_2HBr_5, and C_2Br_6 are 14.7, 17.8, 23.2, 37.1, 53.7, and 86.3 kJ/mol, respectively. The values agree with the available spectroscopic analysis for C_2H_5Br of 11.7,[40] 14.9,[41] and 15.4,[42] for CH_3CHBr_2 of 17.8,[43] and for CH_3CBr_3 of 23.0 kJ/mol,[44] etc. The estimated barrier height of 83.0 kJ/mol for C_2Br_6 by Kudchadker and Kudchaker[18] is also supported by our G3X calculations. For CH_2BrCH_2Br, $CH_2BrCHBr_2$, and $CHBr_2CHBr_2$, two stable rotamers, which are distinguishable from spectroscopic study,[45] are separated by two different torsion barriers with the lowest rotamers of *trans* (dihedral angle BrCCBr = 180°), *asym* (BrCCH = 51.9°), and *gauche* (HCCH = 65.3°), respectively (Figure 1). The energy difference between the two rotamers of CH_2BrCH_2Br has been determined as 7.0 ± 0.5, 6.4, or 5.8 kJ/mol from spectroscopic analysis,[46] agreeing with the G3X value of 6.9 kJ/mol. An activation energy of 12.6 ± 2.1 kJ/mol from the *gauche* to the *trans* rotamer of CH_2BrCH_2Br has also been obtained by Takagi et al.[47] from ultrasonic relaxation measurement, and the G3X barrier height of 14.1 kJ/mol is within the experimental uncertainty range. For $CHBr_2CHBr_2$, Carlson et al. obtained a relative stability of 2.8 ± 0.6 kJ/mol in liquid state from spectroscopic analysis,[48] being supported by G3X prediction of 3.0 kJ/mol. Two barriers of 1730 and 3026 cm^{-1} relative to the *gauche* rotomer are also computed using the energy difference between the two stable conformers and the two torsion frequencies.[48] These values are much lower than the G3X predictions of 2541 and 4735 cm^{-1}, respectively.

Contributions to the thermodynamic functions, including entropy, heat capacity, and enthalpy due to the internal rotations in bromoethanes, are obtained from the calculated energy levels using the G3X potential energy curve, while the contributions from other vibrational modes and overall rotation are evaluated using RRHO approximation. Note that summation over the torsion levels implies the inclusion of contributions to thermodynamic parameters from higher rotamers for CH_2BrCH_2Br, $CH_2BrCHBr_2$, and $CHBr_2CHBr_2$. The results are listed in Table 2, along with the comparisons to previous calculations and measurements. Current calculations on the entropy and heat capacity of C_2H_6 agree with the evaluated values[8] within 1 J K^{-1} mol^{-1} up to 1500 K, being slightly better than previous predictions using a similar numerical procedure.[49] For CH_2BrCH_2Br, the calculated C_P values of 96.12, 101.90, and 107.05 J K^{-1} mol^{-1} at 383, 428, and 473 K also agree with the experimental values of 96.82, 102.80, and 108.20 J K^{-1} mol^{-1}, respectively, where the estimated contributions from internal rotation are 15.56, 15.23, and 14.75 J K^{-1} mol^{-1} with the present torsion potential versus 16.00, 15.77, and 15.36 J K^{-1} mol^{-1} with the simplified torsion potential containing V_1 and V_3 terms only.[50] No experimental result can be found for other bromoethanes. Alternatively, values have been estimated for CH_3CH_2Br, CH_3CHBr_2, CH_3CBr_3, and C_2Br_6 by Kudchadker and Kudchadker using experimental and estimated vibrational frequencies[18] and for C_2HBr_5 and C_2Br_6 by Oren et al. using B3LYP/Aug-VTZ geometries and vibrational frequencies.[10] For CH_3CH_2Br and CH_3CHBr_2, our predicted entropies and heat capacities agree within 1.5 J K^{-1} mol^{-1} with those by Kudchadker and Kudchadker,[18] while for CH_3CBr_3, C_2HBr_5, and C_2Br_6, our predictions are higher than previous ones by 2−5 J K^{-1} mol^{-1}. The differences are largely due to the lower vibrational frequencies used in the present study, and increase with the degree of bromination.

The enthalpies of formation of bromoethanes obtained from G3X atomization energies and isodesmic reaction R1 are summarized in Table 1. There has been no experimental determination of the enthalpies of formation of 1,1-$C_2H_4Br_2$, 1,1,1-$C_2H_3Br_3$, 1,1,2,2-$C_2H_2Br_4$, C_2HBr_5, and C_2Br_6. The corrections to the atomization procedure using isodesmic reaction R1 are again minor since the enthalpy of formation of C_2H_6 from G3X atomization energy agrees excellently with the experimental value. The following discussion will be based on the enthalpies of formation obtained from R1.

Lane et al.[51] first obtained $\Delta_f H^\circ_{298K}(C_2H_5Br) = -64.6$ kJ/mol and Cox and Pilcher[37] later adjusted it to −63.6 ± 2.1 kJ/mol from the measured enthalpy change of reaction $C_2H_4 + HBr \rightarrow C_2H_5Br$. The measured $\Delta_r H^\circ_{298K} = -80.3 \pm 2.1$ kJ/mol agrees with the G3X prediction of −82.7 kJ/mol, which is just outside the experimental uncertainty. $\Delta_f H^\circ_{298K}$ of −61.9 ± 1.0 and −65.3 ± 6.3 kJ/mol are also obtained from the enthalpy of hydrogenation reaction $C_2H_5Br + H_2 \rightarrow C_2H_6 + HBr$,[30,52] for which the experiment measures $\Delta_r H^\circ_{298K} = -59.0 \pm 1.1$ kJ/mol, comparing to the G3X prediction of −52.7 kJ/mol. $\Delta_f H^\circ_{298K}(C_2H_5Br)$ of −65.0 and −65.3 kJ/mol from the present G3X predictions using the atomization and isodesmic reaction R1 are within the uncertainty range of Cox and Pilcher's recommendation.

Kudchaker and Kudchaker have estimated $\Delta_f H^\circ_{298K}$(1,1-$C_2H_4Br_2$) = −41.0 ± 4.6 kJ/mol from the group additivity method.[18] Experimentally, $\Delta_f H^\circ_{298K} = -32.2$ kJ/mol can be obtained from the measured $\Delta_r H^\circ_{298K} = 70 \pm 3$ kJ/mol for reaction 1,1-$C_2H_4Br_2 \rightarrow C_2H_3Br + HBr$[53] with $\Delta_f H^\circ_{298K}(C_2H_3Br) = 74.1 \pm 3.1$ kJ/mol.[38] The measured enthalpy of reaction is supported by the G3X value of 75.4 kJ/mol, and the enthalpy for 1,1-C_2H_3Br is supported by the G3X values of −38.2 and −38.8 kJ/mol using atomization and isodesmic reaction R1.

For 1,2-$C_2H_4Br_2$, two rotamers are distinguishable from spectroscopic study; while attempts for its enthalpy of formation through combustion study were not conclusive because of the large discrepancies on the heat of combustion of liquid by ca. 25 kJ/mol and on the enthalpy of vaporization by ca. 7 kJ/mol.[45] On the other hand, $\Delta_f H^\circ_{298K}$ (1,2-$C_2H_4Br_2$) = −42.2 kJ/mol can be derived from $\Delta_r H^\circ_{298K} = 80 \pm 2$ kJ/mol for 1,2-$C_2H_4Br_2 \rightarrow C_2H_3Br + HBr$,[53] with which the corresponding G3X $\Delta_f H^\circ_{298K} = -43.8$ kJ/mol using R1 and $\Delta_r H^\circ_{298K} = 80.0$ kJ/mol agree excellently. Equilibrium study found that 1,2-$C_2H_4Br_2$ is more stable than 1,1-$C_2H_4Br_2$ by 13.1 kJ/mol[37,54] or by 10 kJ/mol from the measured $\Delta_r H^\circ_{298K} = 70 \pm 3$ kJ/mol for 1,1-$C_2H_4Br_2 \rightarrow C_2H_3Br + HBr$,[53] being higher than the G3X difference of 5.0 kJ/mol (298 K) or 5.5 kJ/mol (0 K).

No experimental measurement is available on $\Delta_f H^\circ(CH_3CBr_3)$. Kudchaker and Kudchaker's group-additivity estimation of $\Delta_f H^\circ_{298K} = -4.6$ kJ/mol[18] agrees reasonably with our G3X prediction of −0.4 kJ/mol. Experimental measurement is not available for $\Delta_f H^\circ(CH_2BrCHBr_2)$, but it is interesting to compare the G3X calculation with the recent TPEPICO study on $CH_2BrCHBr_2$.[38] The G3X adiabatic IP(C_2H_3Br) of 9.824 eV is in excellent agreement with the experimental values of 9.8171 ± 0.0006 eV[55] or 9.8200 ± 0.0015 eV,[14] and the G3X AE($C_2H_3Br_2^+$ + Br) of 10.683 eV is only slightly higher than the experimental value of 10.608 ± 0.008 eV,38 while the measured AE($C_2H_2Br^+$ + Br + HBr) of 12.301 eV is higher than our G3X prediction of 12.06 eV for CH_2CBr^+ + Br + HBr, indicating a possible exit barrier.

There is no experimental measurement on the enthalpies of formation of $C_2H_2Br_4$, C_2HBr_5, and C_2Br_6. Kudchaker and Kudchaker have used the bond-additivity method to estimate $\Delta_f H^\circ_{298K}$ values of 33.1 ± 7.5, 79.5 ± 10.5, and 133.1 ± 15.1 kJ/mol for CH_2BrCBr_3, C_2HBr_5, and C_2Br_6,[18] respectively, agreeing within their uncertainty with (while being systematically higher than) our G3X values of 30.9, 71.2, and 121.0 kJ/mol using isodesmic reaction R1. Oren et al.'s calculations of 113.1 and 165.5 kJ/mol at the DK-CCSD(T)/Aug-VTZ level for C_2HBr_5 and C_2Br_6[10] are much higher than the present G3X predictions and values by Kudchaker and Kudchaker.

E. Comparison of Previous Predictions. The enthalpies of a few species of C1 and C2 brominated compounds have been predicted previously at the QCISD(T)/6-311+G(3df,2p)[9] and CCSD(T)/Aug-VTZ[10] levels using isodesmic reaction R1. Both calculations predict significantly higher enthalpies of formation for the available compounds than the present G3X calculations, especially for highly brominated species such as $CHBr_3$, CBr_4, and C_2Br_6. The fact that our G3X values are systematically lower is probably due to the different inclusion of core–electron correlation. The QCISD(T)/6-311+G(3df,2p) uses Hay–Wadt relativistic ECP to represent [Ar]3*d*10 for Br, and the DK-CCSD(T)/Aug-VTZ calculation also has a large core of [Ar] for Br. The QCISD(T)/6-311+G(3df,2p)-ECP results differs only slightly from full Gaussian-2 calculations, e.g., $\Delta_f H^\circ_{298K}(CHBr_3) = 51.6$ kJ/mol and $\Delta_f H^\circ_{298K}(CBr_4) = 110.6$ kJ/mol using isodesmic reaction R1 are consistent with our values of 49.8 and 109.2 kJ/mol at the G2(Full)+ZPE//MP2/6-31G(d,p) level, respectively.[9] The values are further lowered to 43.5 and 95.3 kJ/mol at the G3X level.

In G3X, the QCISD(T)/6-31G(d) calculation has cores of [Ar] for Br and [He] for C, and the core correlation is extrapolated to all inner electrons at the MP2 level. Intensive W2DK calculations have also been carried out on a few compounds as benchmarked by Oren et al.[10] For CH_3Br and CH_2Br_2, G3X agrees with W2DK, e.g., the G3X atomization energies of 1498.7 and 1356.4 kJ/mol agree with the W2DK values of 1497.9 and 1352.6 kJ/mol (with the same ZPE corrections),[10] while the discrepancies for CBr_4, C_2HBr, and C_2Br_2 are large, e.g., G3X atomization energies of 1057.4, 1475.7, and 1328.2 kJ/mol versus W2DK values of 1034.5, 1464.6, and 1311.5 kJ/mol, respectively. For the enthalpies of formation of C_2HBr_3, C_2Br_4, C_2HBr_5, and C_2Br_6, the G3X predictions are also significantly lower than those at the CCSD(T)/Aug-VTZ level. On the other hand, G3X predictions support the group additivity estimations for bromoethanes by Kudchadker and Kudchadker within their uncertainty ranges.[18]

Conclusion

Thermodynamic properties of closed-shell C1 and C2 brominated hydrocarbons have been predicted using G3X model chemistry with the internal rotations in ethanes treated quantum mechanically. The G3X enthalpies of formation obtained from atomization and/or isodesmic reactions are in excellent agreement with the well-established experimental values for CH_3Br, CH_2Br_2, and C_2H_3Br. G3X calculations are also in close agreement with previous DK-CCSD(T)/Aug-VTZ predictions[10] on CH_3Br and CH_2Br_2, while being systematically lower for other species including $CHBr_3$, CBr_4, C_2HBr, C_2Br_2, C_2HBr_3, C_2Br_4, C_2HBr_5, and C_2Br_6.

Acknowledgment. We are thankful for the services of the grid computing platform SCUTGrid provided by the Information Network Research and Engineering Center of the South China University of Technology. We are also thankful for the helpful discussions with Professor Thomas Baer of the University of North Carolina and Professor Weidong Zhou of Zhejiang Normal University.

Supporting Information Available: The molecular parameters used in the evaluation of thermodynamic properties are listed in Tables S1 and S2. The ZPE corrections, G3X electronic energies and atomization energies, and the thermal corrections at 298 K are listed in Table S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP0774443