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Theoretical study of bromine halocarbons: Accurate enthalpies of formation

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ABSTRACT

The gas phase enthalpies of formation of sixty-five C_1 and C_2 bromine compounds have been calculated using G3, G4, the correlation consistent Composite Approach (ccCA) and CCSD(T)/CBS. Several compounds investigated have importance in atmospheric chemistry due to their global warming potentials. Compounds investigated include chlorine and fluorine containing bromine compounds, and bromine hydrocarbons. Computational methods have been compared to experimental and theoretical values when available. All methods investigated calculate enthalpies of formation that are in agreement with available ATcT, each with a greater than 0.999 R^2 value and mean absolute deviations (MADs) of 1.2 kcal/mol, 0.6 kcal/mol, 0.7 kcal/mol, and 0.6 kcal/mol for G3, G4, ccCA, and CCSD(T), respectively. The importance of molecular spin-orbit corrections is noted. The molecular spin-orbit correction for tetrabromomethane increased the enthalpy of formation by 2.7 kcal/mol to an enthalpy of formation of 27.5 kcal/mol when using CCSD(T)/CBS.

1. Introduction

Greenhouse gases (GHGs) play a major role in environmental issues, such as global warming and ozone depletion. Much research has been done on high impact GHGs including carbon dioxide (CO_2), methane (CH_4), and ozone (O_3); however, halocarbons, which are considered low impact GHGs, pose a greater threat on future atmospheric trends than high impact GHGs due to their long lifetimes and region of IR absorption. Bromine halocarbons have lifetimes that range from 2.5 years for CBr_2F_2 to 72 years for $CBrF_3$ [1–3]. Bromine halocarbons are found in flame retardants (BFRs), marine aerosols, and pesticides [4–9]. BFRs are present in plastics and foams, and when these are degraded thermally, the concern of hazardous products forming is increased [6].

The study of brominated halocarbons is of great importance due to the impact that bromine has on the atmosphere. Although bromine halocarbons are stable until they reach the upper atmosphere, ultraviolet light causes bromine halocarbons to break down, forming bromine radicals [1,3,10–12]. These bromine radicals, similar to chlorine radicals, act as a catalyst for the breakdown of ozone (O_3). Bromine atoms break down ozone into O_2, and they also produce bromine oxides which can then interact with oxygen atoms and form O_2 and recycle the bromine (Fig. 1) [8]. This is similar to the interaction cycle of a single chlorine atom with ozone which can be responsible for the breakdown of thousands of ozone molecules [13].

Both experimental and computational research is being conducted to further understand the effect of bromine atoms on molecular properties [6,8,9,14–17]. Enthalpies of formation are of particular interest for bromine halocarbons as they can be used to make chemistry-climate models [18,19], which help in understanding and predicting their effects on climate change. It is important to have accurate properties for use in climate prediction models, and validation of theoretical approaches is necessary. Due to the absence of experimental information available and the large deviations that plague the available experimental data for halocarbons, theoretical approaches have been used more widely to study atmospheric compounds and are becoming a primary source for accurate thermochemical properties of atmospheric compounds [16]. However, theoretical calculations become increasingly rigorous going down the periodic table due to increasing electron count and scalar relativistic effects. Additional care also must be taken for bromine containing halocarbons as the reference state for elemental bromine, Br_2, is liquid, not gas. Previous computational studies have been done on third row containing molecules using composite methods including the Gaussian-n methods (G*n*) and the correlation consistent Composite Approach (ccCA), along with other high level calculations including CCSD(T)/CBS [6,15,17,20,21]. An investigation on fifty-one molecules containing third row atoms (Ga-Kr) using the ccCA, G3, and G4 methods to calculate enthalpies of formation, atomization energies, ionization potential, electron affinities, and proton affinities, had mean absolute deviations (MADs) when comparing to experiment of

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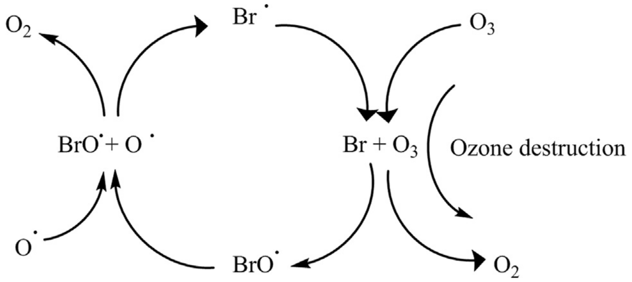

Fig. 1. Scheme of bromine halocarbon compounds interaction in the stratosphere.

0.95 kcal mol^{-1}, 1.07 kcal mol^{-1}, and 0.86, respectively [21]. G4 was shown to provide values closest to experiment, possibly due to the empirical parameterization within the higher level correction (HLC) which contains experimental values for third row species in the G4 methodology, improving on the previous G*n* methodologies [21]. The ccCA method had an average by ± 0.95 kcal/mol from experiment without the use of such empirical parameterization. Incorporating imaging photoelectron photoion coincidence spectroscopy (iPEPICO) with ab initio calculations and a thermochemical network, Bodi et al. [14] updated enthalpies of formation for a series of CF_nBr_{4-n} (n = 0–3) compounds, commenting on the importance of available accurate data for halocarbons and finding the misreported enthalpy of formation value of ClF causing erroneous results. Such misreported information attests to the use of non-empirical based quantum mechanical approaches to remove the reliance on inconsistent or unavailable experimental values. Investigations on C_1 and C_2 bromo hydrocarbons and radicals by Oren et al. [17] used W2DK, a computationally expensive methodology known for predicting energetic properties with kJ/mol accuracy, for eight of the nineteen compounds investigated. Isodesmic reactions were used to determine enthalpies of formation using DK-CCSD(T)/Aug-VTZ, and G2 for comparison. Enthalpies of formation calculated were assumed to be within 1 kcal/mol or less due to methodology extensive benchmarking [17]. Twenty-one closed shell bromo C_1 and C_2 hydrocarbons were investigated by Wang [22] using the G3X composite method. Comparing to the W2DK values of Oren et al. [17] showed G3X to underestimate the enthalpies of formation, having an increase in deviation from the W2DK values with increasing bromine atoms, although for several compounds agreeing with previously reported group additivity derived enthalpies of formation by Kudchadker [23,24]. Dávalos et al. [15] investigated bromine and chlorine halomethanes using the G3 and G4 composite methods. Enthalpies of formation were calculated with atomistic and isodesmic approaches showing that G4 leads to accurate enthalpies of formation for brominated and chlorinated compounds [15]. Kolesov and Papina [25] proposed theoretical values for 210 haloethanes containing C, H, F, Cl, and Br, using a least squares method, noting that enthalpies of formation of compounds containing bromine were suggested to have an error bar of not more than 6 kcal/mol. Experimental and theoretical enthalpies of formation are limited in the literature for C_2 bromo compounds containing chlorine and/or fluorine, in many cases not having any reported values.

This study calculates the enthalpies of formation for sixty-five C_1 and C_2 bromine hydrocarbons. Halon 2402 ($C_2F_4Br_2$), Halon 1301 (CF_3Br), FC-11B3 ($CFClBr_2$), and Halon-1011 (CH_2ClBr) are among the gaseous molecules of interest. We have used G3, G4, ccCA among the different composite methods and CCSD(T)/CBS for calculations. The calculated heats of formations at CCSD(T)/CBS have been compared against the results obtained with composite methods and experimental values.

2. Computational methods

Composite methods used in this study are Gaussian-3 (G3) [20,26], Gaussian-4 (G4) [27,28], and ccCA [21,29]. A CCSD(T) with a complete basis set CBS extrapolation method including corrections for scalar relativistic effects, and core valence correlation is also presented. Equilibrium structures and frequencies were calculated using B3LYP with cc-pVTZ. CCSD(T) single point energies using augmented correlation consistent polarized valence basis sets (aug-cc-pV*n*Z, where *n* = D, T, Q) were carried out. The cc-pV*n*Z basis sets were developed with the 3d electrons frozen in order to correlate the electrons in the valence 4s and 4p orbitals for third row atoms [30]. Accordingly, the 3d orbitals of bromine were frozen using FreezeG2 for the CCSD(T)/aug-cc-pVnZ calculations. CCSD(T) energies were extrapolated to the CBS limit using the formula (Eq. (1)) proposed by Xantheas and Dunning [31] and Feller [32,33] for the extrapolation of the Hartree-Fock energies:

$$E(n) = E_{\text{HF-CBS}} + B\exp(-Cn) \tag{1}$$

The correlation energies have been extrapolated separately using the Peterson [34] and Schwartz 3 [35–37] methods (Eqs. (2) and (3), respectively), where *n* represents the zeta level of the basis set (n = D, T, Q), and $l_{\max}$ is the highest angular momentum in the basis set. This averaging of extrapolation schemes is carried out to be consistent with the extrapolation scheme used in the ccCA methodology.

$$E(n) = E_{\text{corr-CBS}} + B\exp[-(n-1)] + C\exp[-(n-1)^2] \tag{2}$$

$$E(l_{\max}) = E_{\text{corr-CBS}} + \frac{B}{(l_{\max})^3} \tag{3}$$

The core-core and core-valence correlation (E_{CV}) was included using the aug-cc-pCVTZ basis sets which were constructed to include the 3s, 3p, and 3d electron correlation [38]. This was carried out at the MP2 level of theory using FC1 to freeze the inner noble gas core. Scalar relativistic effects (E_{SR}) were accounted for using a Douglass-Kroll-Hess (DKH) Hamiltonian (MP2-DKH) along with cc-pVTZ-DK basis sets. Zero-point energies (E_{ZPE}) and enthalpy corrections were taken at the B3LYP/cc-pVTZ level and scaled using 0.9889 [39]. First and second order spin orbit (E_{SO}) corrections are included for each atom. The tight-d (+*d*) polarization functions have been included in the Dunning basis sets (cc-pVnZ + *d*, n = D, T, Q) for chlorine atoms [40,41]. The overall energy for CCSD(T)/CBS is (Eq. (4):

$$\begin{aligned} E_{\text{DK-CCSD(T,FC1)}} = {} & E_{CBS}\,[E_{\text{HF-CBS}} + E_{\text{corr-CBS}}] \\ & + E_{CV}\,[\text{MP2/aug-cc-pCVTZ}-\text{MP2/aug-cc-pVTZ}] \\ & + E_{SR}\,[\text{MP2/cc-pVTZ-DK}-\text{MP2/cc-pVTZ}] + E_{ZPE} + \Delta E_{SO} \end{aligned} \tag{4}$$

The CCSD(T)/CBS including scalar relativistic effects, core-core core-valence correlation, ZPE and atomic spin orbit as described above will be referred to as the CCSD(T) or CCSD(T)/CBS method in the results and discussion. Calculations in this study were carried out using the Gaussian16 software package [42]. Scalar relativistic calculations were carried out in the Gaussian09 software package [43]. Composite method energies at 0 K and enthalpy corrections are provided in the Supplemental Material. Spin-orbit corrections for molecules have not been included unless otherwise noted.

2.1. Enthalpies of formation

An atomistic approach (RC0) was used in order to find gas phase enthalpies of formation (ΔH_f) at 298 K.

Table 1

Enthalpies of formation (kcal/mol) for bromine substituted methane.

Name	Formula	G3	G4	ccCA	CCSD(T)	Literature values	ATcT [42]
Bromomethane	CH_3Br	−9.0	−8.3	−9.4	−8.7 [−9.7][a]	−9 ± 0.4 [54], −8.5 ± 0.3 [62], −8.7 ± 0.1 [63], −9.1 ± 0.3 [51]	−8.5 ± 0.1
Dibromomethane	CH_2Br_2	0.0	1.2	−0.1	0.6 [0.6][a]	0.8 ± 0.8 [58], 2.4 ± 3.6 [54], −2.7 ± 1.2 [51], 1.4 ± 1.2 [50], −2.6 ± 2.2 [64], −3.53 [23], 0 ± 1 [65]	0.8 ± 0.3
Tribromomethane	$CHBr_3$	9.9	11.9	10.7	11.4	11.3 ± 0.3 [50], 14.3 ± 3.6 [54], 13.2 ± 0.79 [50], 5.7 ± 1.1 [51,66], 13.2 ± 1.2 [57], 12.97 [17]	11.5 ± 0.3
Bromotrifluoromethane (Freon 1301)	CF_3Br	−157.2	−155.2	−156.2	−156.1	−155.8 ± 0.1 [67], −157.89 [54], −150 [62], −152.2 ± 0.7 [67], −154.72 ± 0.7 [68], −154.6 ± 0.8 [14]	−155.7 ± 0.1
Difluorodibromomethane (Halon-1202)	CF_2Br_2	−93.5	−90.8	−91.8	−91.6	−90.6 ± 1.9 [65], −86.3 ± 1.8 [14]	−91.9 ± 0.3
Tribromofluoromethane	$CFBr_3$	−33.5	−30.6	−31.4	−31.0	−34.29 [23][b], −26.7 ± 1.8 [14]	−31.5 ± 0.4
Bromotrichloromethane	CCl_3Br	−12.8	−11.3	−11.1	−10.9	−10 ± 0.3 [69], −9.4 ± 2.0 [62,68], −9.3 [23][b]	−10.3 ± 0.2
Dibromodichloromethane	CCl_2Br_2	−1.1	0.8	0.8	1.1	2.22 [23][b]	0.9 ± 0.4
Tribromochloromethane	$CClBr_3$	10.5	12.8	12.6	13.0	11.65 [23][b]	12.7 ± 0.4
Tetrabromomethane	CBr_4	22.1	24.8	24.3	24.8 [27.5][a]	28.7 ± 3.6 [54], 20.1 ± 0.81 [51], 28 ± 1 [50], 12 [67], 18.9 [52], 35.1 [70], 28.49 [17][c], −27.2 ± 1.0 [14]	24.3 ± 0.3
Bromochlorofluoromethane	$CHFClBr$	−56.0	−54.5	−55.7	−55.3	−54.93 [23][b]	−55.4 ± 1.3
Dibromochlorofluoromethane (FC-11B3)	$CFClBr_2$	−45.8	−43.3	−44.0	−43.7	−43.73 [23][b]	−44.8 ± 1.3
Bromochlorodifluoromethane (Halon-1211)	CF_2ClBr	−106.4	−104.3	−105.2	−105.0	−104.02 [23][b]	−105.7 ± 1.3
Bromodichlorofluoromethane (FC-11B2)	$CFCl_2Br$	−58.2	−56.1	−56.7	−56.5	−55.00 [23][b]	−57.4 ± 1.3
Bromodifluoromethane (HBFC-22B1)	CHF_2Br	−102.6	−101.0	−102.3	−102.0	−102.66 [23][b]	−101.4 ± 0.1
Bromofluoromethane	CH_2FBr	−51.1	−49.9	−51.3	−50.6	−51.20 [23][b]	−50.8 ± 1.3
Dibromofluoromethane (FC-21B2)	$CHFBr_2$	−43.6	−41.6	−42.9	−42.4	−45.80 [23][b]	−42.9 ± 1.3
Bromochloromethane (Halon-1011)	CH_2ClBr	−11.0	−10.3	−11.6	−11.0	−10.5 ± 0.5 [58], −10.8 ± 1.2 [54], −5 ± 2 [71], −10.71 [23][b]	−10.3 ± 0.3
Bromodichloromethane (FC-20B1)	$CHCl_2Br$	−12.9	−11.9	−12.7	−12.4	−11.97 ± 0.43 [57]	−12.0 ± 0.3
Dibromochloromethane	$CHClBr_2$	−1.5	0.1	−0.9	−0.4	0.98 ± 1.17 [57], 2.4 ± 4.8 [54], −2.14 [23][b]	−0.1 ± 0.8

[a] Brackets include molecular spin-orbit corrections from Oren et al. [17].

[b] Estimated using group additivity by Kudchadker and Kudchadker [23].

[c] Calculated by Oren et al. [17] using W2DK and isodesmic reactions.

$$\Delta H_{f,M}(298\,\mathrm{K}) = \sum_{atoms} n\Delta H_{f,A}(0\,\mathrm{K}) - \left(\sum_{atoms} nE_A - E_M - \Delta E_{ZPE}\right) + (H_M(298\,\mathrm{K}) - H_M(0\,\mathrm{K})) - \sum_{atoms} n_A(H_A(298\,\mathrm{K}) - H_A(0\,\mathrm{K})) \quad (5)$$

The enthalpy of formation was calculated using four components as seen in Eq. (5). The first component is the sum of the atom enthalpies ($\Delta H_{f,A}$) at 0 K. The atomic enthalpies of formation ($\Delta H_{f,A}$ (0 K)) of elemental hydrogen, carbon, fluorine, chlorine, and bromine are 51.63 kcal mol^{-1}, 170.11 kcal mol^{-1}, 18.47 kcal mol^{-1}, 28.59 kcal mol^{-1}, and 28.18 kcal mol^{-1} respectively. The second component is the dissociation energy which consists of the energy of the atom (E_A), the energy of the molecule (E_M), and the molecular zero-point energy (ΔE_{ZPE}). The third and fourth components represent the enthalpy correction of the molecule (H_M) and atoms (H_A) respectively.

Three connectivity-based reaction schemes were also used to calculate enthalpies of formation: isogyric, isodesmic, and hypohomodesmotic reactions [44–46]. These reaction schemes capture the change in the local environment along the reaction and are used to calculate the systematic errors in different methods for the respective chemical changes [44–47]. Isogyric (RC1) reactions maintain the number of unpaired electron spins. Isodesmic (RC2) reactions preserve hybridization on each atom. Hypohomodesmotic (RC3) reactions preserve the immediate connectivity of all the atoms in the molecule. An example of each of these is provided below for C_2Br_2.

$$C_2Br_2 + 5H_2 \rightarrow 2CH_4 + 2HBr \quad \text{(RC1)}$$

$$C_2Br_2 + 2CH_4 \rightarrow C_2H_2 + 2CH_3Br \quad \text{(RC2)}$$

$$C_2Br_2 + C_2H_2 \rightarrow 2C_2HBr \quad \text{(RC3)}$$

Enthalpies of formation using reaction schemes were calculated using the difference of the products and reactants enthalpies of formation (ΔH_f) from ATcT and subtracting the difference of the calculated enthalpies (H(298 K)) of the products and reactants (Eq. (6)).

$$\Delta H_{f,M}(298\,\mathrm{K}) = \sum_{prod} n\Delta H_{f,prod}(298\,\mathrm{K}) - \sum_{react} n\Delta H_{f,react}(298\,\mathrm{K}) - \left[\sum_{prod} nH(298\,\mathrm{K}) - \sum_{react} nH(298\,\mathrm{K})\right] + H_M(298\,\mathrm{K}) \quad (6)$$

Enthalpies of formation and enthalpies used for reactants and products are provided in the Supplemental Material, Table S4. Reaction schemes should be used with caution due to large propagation of uncertainty. The limited experimental data and large uncertainties for particular reactants and products may cause an increase in errors using reaction schemes over an atomization approach for composite methods. Composite methods are known to include large cancellation of errors, allowing for accurate properties to be determined using an atomization approach [20,21,26,27,29,47,48].

3. Results and discussion

Tables 1–3 list out the calculated and available experimental enthalpies of formation of brominated compounds. For many of the brominated molecules, the experimental heats of formation are unavailable. Values that are available or have been derived from experiments also show large ranges of deviation between approaches. For example,

Table 2

Enthalpies of formation (kcal/mol) for bromine substituted ethane using the atomization approach. Hypohomodesmotic (RC3) calculated enthalpies of formation are provided in parenthesis.

Name	Formula	G3	G4	ccCA	CCSD(T)	Literature values	ATcT [43]
Bromoethane	C_2H_5Br	−15.7	−14.8	−16.3	−15.1	−15.6 ± 1.5 [72], 15.3 [62], −15.2 ± 0.5 [24]	−15.1 ± 0.1
1,1-Dibromoethane	CH_3CHBr_2	−9.5	−8.1	−9.5	−8.4	−9.8 [24], −6.4 ± 0.5 [25]	−8.7 ± 1.9
1,2-Dibromoethane	$(CH_2Br)_2$	−10.8 (−9.7)	−9.3 (−9.6)	−11.2 (−9.4)	−10.0 (−9.4)	10.1 [73], −9.06 ± 0.35 [68], −9.2 ± 0.3 [25], 7.82 ± 1.9 [60][a]	−9.0 ± 0.3
1,1,2-Tribromoethane	$CHBr_2CH_2Br$	−3.0 (−1.7) (−2.8)[d]	−0.9 (−1.5) (−2.6)[d]	−2.4 (−1.1) (−2.2)[d]	−1.3 (−1.0) (−2.1)[d]	2.7 [25][b]	
1,1,1-Tribromoethane	CH_3CBr_3	−0.6	1.4	0.6	1.7	−1.1 [24], 0.76 ± 1.9 [60][a]	
1,1,2,2-Tetrabromoethane	$(CHBr_2)_2$	6.3 (7.7) (5.5)[d]	9.2 (8.2) (6.0)[d]	7.9 (8.8) (6.6)[d]	9.0 (8.9) (6.7)[d]	15.0 [25][b]	
1,1,1,2-Tetrabromoethane	CBr_3CH_2Br	6.8 (8.6)	9.6 (9.0)	8.9 (9.6)	10.0 (9.7)	16.6 [25][b]	
Pentabromoethane	C_2HBr_5	16.2 (18.2) (17.1)[d]	19.9 (18.9) (17.8)[d]	19.8 (20.1) (19.0)[d]	20.9 (20.3) (19.2)[d]	27.03 [17][c]	
Pentafluorobromoethane	C_2F_5Br	−260.8	−257.1	−257.5	−257.4	−254.4 ± 1 [74]	
1,1-Dibromotetrafluoroethane	CF_3CFBr_2	−202.2	−198.0	−198.4	−198.0	−195.7 [25][b]	
1,2-Dibromotetrafluoroethane	$(CF_2Br)_2$	−198.5	−193.8	−194.3	−193.9	−189.0 ± 1.1 [68], −188.8 ± 1 [75], −196.72 [60][a]	
1,1,2-Tribromo-1,2,2-trifluoroethane	$CFBr_2CF_2Br$	−139.5	−134.5	−134.9	−134.3	−130.0 [25][b]	
1,1,1-Tribromo-2,2,2-trifluoroethane	CF_3CBr_3	−148.4 (−145.1)	−144.3 (−144.2)	−144.3 (−143.2)	−143.8 (−143.1)	−139.0 [25][b]	
1,1,2,2-Tetrabromo-1,2-difluoroethane	$(CFBr_2)_2$	−80.6	−75.4	−75.5	−74.7	−68.6 [25][b]	
1,1,1,2-Tetrabromo-2,2-difluoroethane	CBr_3CF_2Br	−85.4	−80.7	−80.6	−79.9	−72.9 [25][b]	
Pentabromofluoroethane	C_2FBr_5	−26.4	−21.6	−21.1	−20.2	−10.6 [25][b]	
Pentachlorobromoethane	C_2Cl_5Br	−29.7	−26.7	−24.6	−24.1	−20.1 [25][b]	
1,1-Dibromotetrachloroethane	CCl_3CClBr_2	−18.2	−14.8	−12.9	−12.3	−5.4 [25][b]	
1,2-Dibromotetrachloroethane	$(CCl_2Br)_2$	−18.2	−14.8	−12.9	−12.3	−6.6 [25][b]	
1,1,2-Tribromo-1,2,2-trichloroethane	$CClBr_2CCl_2Br$	−6.7	−2.9	−1.2	−0.5	−7.4 [25][b]	
1,1,1-Tribromo-2,2,2-trichloroethane	CCl_3CBr_3	−6.7 (−4.2)	−3.0 (−3.1)	−1.3 (−1.1)	−0.6 (−0.9)	−10.0 [25][b]	
1,1,2,2-Tetrabromo-1,2-dichloroethane	$(CClBr_2)_2$	4.8	8.8	10.4	11.3	20.8 [25][b]	
1,1,1,2-Tetrabromo-2,2-dichloroethane	CBr_3CCl_2Br	4.8	8.8	10.4	11.2	22.1[25][b]	
Pentabromochloroethane	C_2ClBr_5	16.3	20.6	22.1	23.0	38.4 [25][b]	
Hexabromoethane	C_2Br_6	27.8 (30.4)	32.3 (31.4)	33.6 (33.2)	34.6 (33.3)	31.8 [24], 39.55 [17][c]	

[a] Derived using NASA polynomial in Burcat [60] Tables.

[b] Calculated using least squares by Kolesov and Papina [25]. Suggested ± 6 kcal/mol error.

[c] Calculated by Oren et al. [17] using W2DK and isodesmic reactions.

[d] Use −9.8 kcal/mol for ΔH_f of CH_3CHBr_2 from a group additivity method [24] in the RC3 reaction.

compounds important in atmospheric chemistry such as tribromomethane have enthalpies of formation that range from 18.9 kcal/mol predicted by Bernstein [49], 13.2 ± 0.8 kcal/mol when studied by Papina [50], and has been reported as low as 5.7 kcal/mol by Bickerton [51] and 4.1 kcal/mol by Wagman [52]. Several compounds calculated in this study have no experimental or theoretical enthalpies of formation available in the literature, including two of the four acetylenes investigated. The Active Thermochemical Tables ATcT [53] enthalpies of formation values are provided to compare theoretical results. ATcT values are derived from both theoretical and experimental properties using a contribution scheme that is continuously updated as more data becomes available. Comparing the ATcT values to the theoretical values determined in this study, using the atomization approach, it is shown that there is little variability between the composite methods, CCSD(T) methodology, and the ATcT values (Fig. 2). The R squared values for all methods in this study obtained 0.9997–0.9999 correlation, with slopes around 1 and y-intercepts approaching 0 kcal/mol, the largest y-intercept value of 1.158 kcal/mol for G3, which is considered the least rigorous theoretical approach from those in this study (see Supplemental Material Table S3). Of the theoretical approaches used in this study, the CCSD(T)/CBS methodology is the most rigorous of the values reported for the compounds investigated unless otherwise mentioned. Hypohomodesmotic enthalpies of formation are included in Tables 2 and 3 for comparison. Enthalpies of formation using the RC1 and RC2 schemes are provided in the Supplemental Material Table S5, and the overall MADs are in Table 4. When applying connectivity based reactions to calculate enthalpies of formation values are dependent on the experimental or theoretical enthalpies of formation available. Highly accurate enthalpies of formation with low uncertainties must be used in Eq. (6) to produce meaningful results. Results discussed are for the atomization approach unless otherwise mentioned.

3.1 Bromomethanes (Table 1)

For all of the bromomethane compounds investigated, the theoretical values calculated are typically within 1 kcal/mol from the ATcT values. For bromomethane the CCSD(T) calculated ΔH_f of −8.7 kcal/mol is in perfect agreement with a previous study by Oren and coworkers [17] using W2DK obtaining an ΔH_f of −8.71 kcal/mol. More electronegative atoms are shown to decrease the enthalpy of formation with the smallest enthalpy of formation for bromotrifluoromethane. Enthalpies of formation (in Table 1) for CF_3Br are consistent with the ATcT values. Tetrabromomethane is consistent with ATcT; however, this is about 4 kcal/mol off from the values suggested by Gurvich [54], Papina [50], and Oren [17] in previous studies. Oren calculated a value of 28.49 ± 1.5 kcal/mol using W2DK. In this study, the CCSD(T)/CBS scheme predicts a value of 24.8 kcal/mol. A closer look at the CCSD(T) contributions in Fig. 3 shows the magnitude of the core-valence, scalar

Table 3
Enthalpies of formation (kcal/mol) for bromine substituted ethylene and acetylene compounds using the atomization approach. Hypohomodesmotic (RC3) calculated enthalpies of formation are provided in parenthesis.

Name	Formula	G3	G4	ccCA	CCSD(T)	Literature values	ATcT [53]
Bromoethylene	C_2H_3Br	17.2	17.8	17.2	18.1	18.9 ± 0.5 [76], 17.7 ± 0.7 [59]	17.7 ± 0.1
(Z)-1,2-Dibromoethylene	$(CHBr)_2$	23.2 (24.3)	24.3 (24.3)	23.7 (24.6)	24.5 (24.6)	24.1 [22][b], 23.7 ± 1.9 [60][c]	
(E)-1,2-Dibromoethylene	$(CHBr)_2$	22.9 (24.1)	24.0 (24.1)	23.5 (24.3)	24.2 (24.3)	24.4 [22][b], 23.7 ± 1.9 [60][c]	
1,1-Dibromoethylene	CH_2CBr_2	24.0	25.0	24.8	25.6	25.12 [22][b], 26.0[d]	
Tribromoethylene	C_2HBr_3	30.3 (33.0)	32.0 (33.0)	31.9 (33.4)	32.6 (33.5)	32.19 [22][b], 34.46 [17][e]	
Bromotrifluoroethylene	C_2F_3Br	−110.7	−108.6	−109.2	−108.8	−108.7 [77]	
1,1-Dibromodifluoroethylene	CF_2CBr_2	−63.9 (−61.3)	−61.7 (−61.1)	−61.9 (−60.7)	−61.5 (−60.7)		
(Z)-1,2-Dibromo-1,2,-difluoroethylene	$(CFBr)_2$	−58.0	−55.7	−56.0	−55.5		
(E)-1,2-Dibromo-1,2,-difluoroethylene	$(CFBr)_2$	−58.9	−56.5	−56.8	−56.3		
Tribromofluoroethylene	C_2FBr_3	−10.6	−8.2	−8.2	−7.6		
Bromotrichloroethylene	C_2Cl_3Br	5.0	5.9	6.3	6.6		
1,1-Dibromo-2,2,-Dichloroethylene	CCl_2CBr_2	16.2	17.6	17.9	18.4		
(Z)-1,2-Dibromo-1,2,-dichloroethylene	$(CClBr)_2$	16.4	17.8	18.1	18.6		
(E)-1,2-Dibromo-1,2,-dichloroethylene	$(CClBr)_2$	16.2	17.6	18.0	18.5		
Tribromchloroethylene	C_2ClBr_3	27.5	29.4	29.7	30.3		
Tetrabromoethylene	C_2Br_4	38.8 (43.0)	41.1 (43.2)	41.4 (43.6)	42.1 (43.7)	45.43 [17][e,] 51.53 [60][c]	
Bromoacetylene	C_2HBr	65.7	66.0	67.1	67.6 [67.2][a]	64.2 ± 1.5 [61], 67.50 [17][e]	65.9 ± 0.5
Bromofluoroacetylene	C_2FBr	37.4 (38.7) (40.3)[f]	39.0 (38.9) (40.5)[f]	39.8 (39.0) (40.6)[f]	40.2 (39.0) (40.6)[f]		
Bromochloroacetylene	C_2ClBr	65.6 (66.7) (68.3)[f]	66.2 (66.8) (68.4)[f]	67.8 (66.9) (68.5)[f]	68.1 (66.9) (68.5)[f]		
Dibromoacetylene	C_2Br_2	76.1 (77.4) (80.6)[f]	77.1 (77.4) (80.6)[f]	79.1 (77.7) (80.9)[f]	79.6 [79.4][a] (77.7) (80.9)[f]	80.14 [17][e]	77.0 ± 0.9

[a] Brackets include molecular spin-orbit corrections from Oren et al. [17].
[b] Calculated by Wang et al. [22] using G3X with an isodesmic (RC2) reaction.
[c] Derived using NASA polynomials in the Burcat Tables [60].
[d] Value from this study using CCSD(T)/CBS with DK and CV corrections and RC2 scheme.
[e] Calculated by Oren et al. [17] using W2DK and isodesmic reactions.
[f] Use Oren et al. W2DK value of 67.5 kcal/mol for C_2HBr [17] in the RC3 reaction.

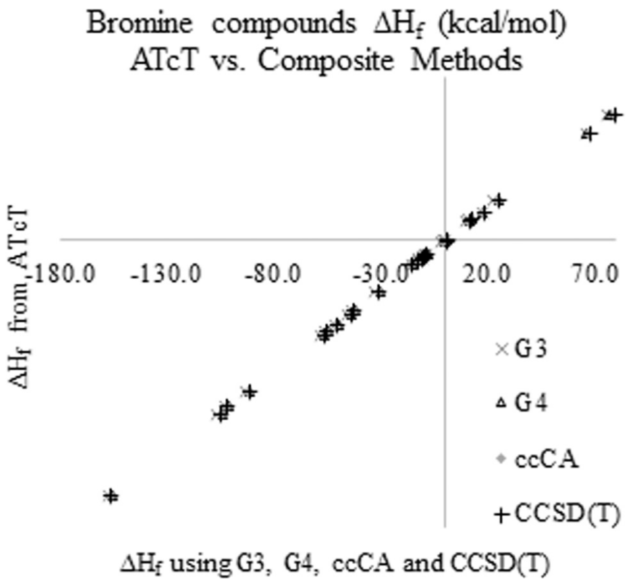

Fig. 2. A comparison of the enthalpies of formation for the 26 bromide compounds that have available ATcT ΔH_f's. These values are compared to the ΔH°_f's calculated from the composite methods, G3, G4, ccCA, and CCSD(T). The corresponding R^2 values and line equations are provided in the Supplemental Material.

relativistic, and CBS extrapolations effects on the enthalpy of formation along with an additional spin-orbit correction for the molecule. Upon further investigation, this deviation can be linked to the spin-orbit correction for the molecule. Including the spin-orbit correction for CBr_4, −14.05 kcal/mol [17,55,56], in the CCSD(T)/CBS energy calculation the enthalpy of formation for tetrabromomethane is 27.5 kcal/mol, which is consistent with the previous values. Shuman [57] and Lago [58,59] have used experiment and theoretical networks to derived enthalpies of formation for several additional brominated methane compounds. The theoretical approaches in this study agree with the predicted values with exception to the bromoform ($CHBr_3$) predicted by Shuman to be 13.2 ± 1.2 kcal/mol [57], and using CCSD(T)/CBS in this study to be 11.4 kcal/mol. The enthalpy of formation of 12.97 kcal/mol determined in Oren et al. [17] using and isodesmic reaction with DK-CCSD(T)/Aug-VQZ agrees with the Shuman proposed value. Experimental enthalpies of formation are not present for compounds containing both chlorine and fluorine, however, values derived using a group additivity method by Kudchadker and Kudchadker [23] are shown to be in agreement with the values calculated in this study, with larger deviations for compounds containing more bromine atoms. $CFBr_3$ and $CHFBr_2$ both differ by more than 3 kcal/mol comparing the CCSD(T)/CBS to the predicted values of Kudchadker and Kudchadker [23]. This deviation provides insights into the importance of spin-orbit correction towards the enthalpy of formation of these two compounds.

3.2 Bromoethane (Table 2)

Brominated closed-shell C_2 compounds were found to have less literature values available compared to the C_1 compounds. The enthalpy of formation of bromoethane of −16.3 kcal/mol using ccCA underestimates the enthalpy of formation compared to the −15.1 kcal/mol with CCSD(T)/CBS. The CCSD(T) values is in agreement with the literature values. G4 overestimates the value with a bromomethane enthalpy of formation of −14.8 kcal/mol. The ATcT value for 1,2-dibromoethane deviates from the values of G3, ccCA, and CCSD(T), while it seems to be in alignment with the G4 calculated value of −9.3 kcal/mol, probably due to the empirical parameterization of the HLC for third row compounds included in the G4 methodology. Pentabromoethane's enthalpy of formation was calculated in this study to be 20.9 kcal/mol using CCSD(T)/CBS which is in disagreement with

Table 4
The MSD, Max Dev., and MAD (kcal/mol) for enthalpies of formation calculated using G3, G4, ccCA, and CCSD(T)/CBS methods with the RC0, RC1, and RC2 schemes, compared to ATcT values.

	G3			G4			ccCA			CCSD(T)		
	RC0	RC2	RC1	RC0	RC2	RC1	RC0	RC2	RC1	RC0	RC2	RC1
MSD	−1.2	−0.8	−2.1	0.5	−0.1	−1.5	−0.3	1.2	0.7	0.2	1.2	0.8
Max dev	2.5	3.4	4.3	1.5	1.8	4.0	2.2	2.7	2.3	2.6	2.7	2.7
MAD	1.2	0.8	2.1	0.6	0.6	1.5	0.7	1.3	1.0	0.6	1.2	1.0

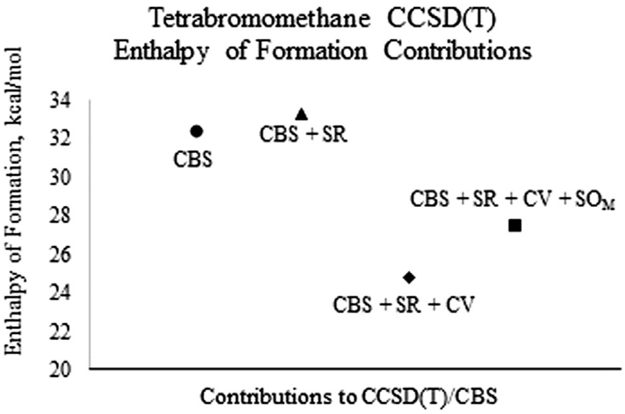

Fig. 3. Enthalpy of formation calculated the complete basis set extrapolation (CBS), scalar relativistic effects (SR), core-valence contributions (CV), and the molecular spin orbit (SO_M) for the CCSD(T)/CBS enthalpy of formation. ZPVE is included throughout.

the 27.03 kcal/mol value using DK-CCSD(T)/Aug-VTZ with an isodesmic reaction calculated previously by Oren [17]. Using the hypohomodesmotic approach the value decreases to 20.3 kcal/mol. The RC3 approach is dependent on the accuracy of the enthalpies of formation for CH_3CBr_3, CH_3CHBr_2 which have little available data and high uncertainties. For CH_3CBr_3, the value is not in ATcT so a value of 0.76 ± 1.9 kcal/mol was used for the enthalpy of formation which was derived using NASA polynomials in the Burcat Tables [60]. CH_3CHBr_2 has a ΔH_f of −8.7 ± 1.9 kcal/mol in ATcT, and −9.8 kcal/mol using group additivity methods. Both enthalpies of formation are presented noting the large dependency on accurate enthalpies of formation for components used in reaction schemes. The ATcT value of −8.7 kcal/mol should be utilized as it agrees with high level calculations in this work for CH_3CHBr_2. Using the ATcT value, the pentabromoethane enthalpy of formation of 20.3 kcal/mol is calculated using RC3 with the CCSD(T) approach, in agreement with the atomization approach enthalpy of formation of 20.9 kcal/mol. Table 2 shows enthalpies of formation tend to increase with increasing the number of bromine atoms and decreasing the number of electronegative atoms. As such, the most positive enthalpy of formation calculated is hexabromoethane with an enthalpy of formation of 34.6 kcal/mol using CCSD(T)/CBS, and the most negative ΔH_f of −257.4 kcal/mol for bromopentafluoroethane. Enthalpies of formation calculated with G4, ccCA, and CCSD(T) are considered to be within, on average, ± 1 kcal/mol from the experimental values.

3.3 Bromoethylene and bromoethyne (Table 3)

The enthalpies of formation for bromine substituted ethylene and acetylene compounds ΔH_f calculated are in agreement between methodologies for bromohydroethylenes, deviating more from one another when including chlorine or fluorine and for the acetylene compounds, going from ethylene to acetylene, having deviations between G3 and CCSD(T)/CBS of 3.5 kcal/mol for C_2Br_2. These deviations between composite methods are shown to greatly reduce with the use of RC3.

The cis and trans isomers of 1,2-dibromoethylene have equivalent enthalpies of formation which is due to the interconversion enthalpy between the two isomers. They are both in good agreement with the derived enthalpy of formation using NASA polynomials in Burcat Tables [60]. Tetrabromoethylene has no experimental values for comparison; but, Oren et al. [17] used a DK-CCSD(T)/Aug-VTZ isodesmic calculation resulting in an enthalpy of formation of 45.43 kcal/mol. This value is slightly higher than the enthalpy of formation of 42.1 kcal/mol using CCSD(T)/CBS. RC3 using CCSD(T) calculates an enthalpy of formation of 43.7 kcal/mol for C_2Br_4. For this reaction CH_2CBr_2 enthalpy of formation was needed. The literature value available is from a G3X isodesmic reaction by Wang et al. of 25.12 kcal/mol. Higher levels of theory are being investigated in this study. A value of 26.0 kcal/mol is used for CH_2CBr_2 in the RC3 reactions. This value was calculated using the CCSD(T)/CBS method and the RC2 reaction.

The calculated heat of formation for bromoacetylene was calculated to be slightly larger than the 64.2 ± 1.5 kcal/mol measured by Okabe [61]. The value of 67.6 kcal/mol predicted using CCSD(T)/CBS in this study is, however, in perfect agreement with the 67.5 kcal/mol calculated by Oren using W2DK [17]. Due to the agreement between the methodologies, both the ATcT value (65.9 kcal/mol) and Oren value (67.5 kcal/mol) for C_2HBr have been used in the RC3 reactions to calculated the enthalpies of formation of the bromohaloacetylenes. 97.3% of the contribution in ATcT to the 65.9 kcal/mol enthalpy of formation for C_2HBr is from G3 and G3B3 calculations. The Oren value using the W2DK method is considered to be more precise for use in RC3 schemes. No literature values are available for bromofluoroacetylene or bromochloroacetlyene, and the values predicted in this study using CCSD(T) are 40.2 and 68.1 kcal/mol respectively. RC3 with CCSD(T) produces enthalpies of formation of 40.6 and 68.5 kcal/mol for C_2FBr and C_2ClBr, respectively. These values are in agreement with the G3, G4, and ccCA methodologies presented using RC3. Dibromoacetylene has an ATcT value of 77 kcal/mol which is in agreement with the G3 (76.1 kcal/mol) and G4 (77.1 kcal/mol) methods, and slightly larger than the 75.8 kcal/mol calculated using G3X and isodesmic reactions in a study by Wang [6]. The ATcT value for C_2Br_2 is also largely based on G3 and G3B3 calculations, contributing over 94.4% to the enthalpy of formation. However, the ccCA (79.1 kcal/mol) and CCSD(T)/CBS (79.6 kcal/mol) methods calculate slightly larger enthalpies of formation that are in agreement with the 80.14 kcal/mol suggested by Oren W2DK calculations. Using the spin-orbit correction for the molecule the enthalpy of formation for C_2Br_2 is 79.4 kcal/mol, again in good agreement with ccCA and CCSD(T)/CBS with little effect from spin-orbit correction. Spin-orbit for the molecule was also shown to only decrease the enthalpy of formation by 0.4 kcal/mol for C_2HBr. The RC3 enthalpy of formation using CCSD(T) is 80.9 kcal/mol when using the Oren predicted value for C_2HBr.

The mean signed deviation (MSD), maximum absolute deviation (Max Dev.), and mean absolute deviation (MAD) for the enthalpies of formation using atomistic (RC0), isodesmic (RC2), and isogyric (RC1) reactions are provided in Table 4. RC0 produced enthalpies of formation using G4, ccCA, and CCSD(T) with MADs from ATcT values of 0.6, 0.7, and 0.6 kcal/mol respectively. G3 enthalpies of formation had an MAD of 1.2 kcal/mol from ATcT when utilizing the atomization approach, and was the only method to decrease MAD when using the RC2 reactions. RC1 reaction schemes were shown to increase the MAD for all methods having MADs of 2.1, 1.5, 1.0, and 1.0 kcal/mol for G3, G4, ccCA, and CCSD(T), respectively. The inherent cancellation of errors in composite methods enable the atomization approach to provide accurate enthalpies of formation for the bromine compounds investigated using G4, ccCA, and CCSD(T).

4. Conclusions

Gas phase enthalpies of formation at 298 K for sixty-five closed shell bromine C_1 and C_2 compounds have been calculated using several theoretical approaches including G3, G4, ccCA, and a CCSD(T) scheme. Scalar relativistic and core valence contributions to the CCSD(T)/CBS were included to ensure accurate predictions. Importance of spin-orbit corrections for the molecule is noted for CBr_4 which increased the enthalpy of formation by 2.7 kcal/mol. Enthalpies of formation have been presented for several C_2 bromine compounds that have no available experimental enthalpies of formation. Isogyric, isodesmic, and hypohomodesmotic enthalpies of formation are presented. Isogyric and isodesmic reaction schemes tend to not increase accuracy for composite methods investigated, although provide method validation with the limited experimental and theoretical data available for the compounds investigated. These reaction schemes should be used with caution as large propagation of uncertainties occurs and are dependent on accurate component (i.e., reactant and product) enthalpies of formation. It is important to have accurate and precise enthalpies of formation for reactants and products when using reaction schemes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.comptc.2018.08.016.

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