

Standard Molar Enthalpies of Formation of Halomethanes Based on Quantum Chemical Computations

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ABSTRACT

Accurate calculations of standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ and carbon-halogen bond dissociation enthalpies, BDE, of a variety of halomethanes with relevance on several atmospheric chemical processes and particularly to ozone destruction, were performed in the gas phase at 298.15 K. The $(\Delta H_f^\circ)_{m(g)}$ of the radicals formed through bond dissociations have also been computed. Ab initio computational methods and isodesmic reaction schemes were used. It is found that for the large majority of these species, the gold standard method of quantum chemistry (CCSD(T)) and even MP2 are capable to predict enthalpy values nearing chemical accuracy provided that isodesmic reaction schemes are used. New estimates for standard molar enthalpies of formation and BDE are suggested including for species that to our knowledge there are no experimental $(\Delta H_f^\circ)_{m(g)}$ (CHCl_2Br , CHBr_2Cl , CHBrCl , CHCl , CHIBr) or BDE values (CHCl_2Br , CHBr_2Cl , CHBrCl , CHCl , CHIBr) available in the literature. The method and calculational procedures presented may profitably be used to obtain accurate $(\Delta H_f^\circ)_{m(g)}$ and BDE values for these species.

INTRODUCTION

A plethora of factors has generated considerable interest in recent years in establishing highly accurate standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$, bond energies and heat capacities. Among these are the following: i) the advances in quantum mechanical calculations which are now capable of achieving $\pm 1 \text{ kJ mol}^{-1}$ accuracy for small molecules¹⁻⁴ ii) prediction of thermochemistry is crucial for designing chemicals with new functionality since fundamental properties of compounds such as enthalpy, heat capacity, standard entropy and Gibbs free energy are needed to understand stability and/or reactivity⁵⁻⁸ iii) accurate, reliable and internally consistent thermochemistry is a necessary condition in many fields of physical chemistry, ranging from kinetics and reaction mechanisms to flames and atmospheric chemistry⁹ iv) the emergence of the active thermochemical tables – that are based on experimental data and theoretical calculations - a novel approach of how to obtain accurate, reliable, and internally consistent thermochemical values and the fact that are rapidly becoming the archetypal approach to thermochemistry⁹ v) several databases containing relevant thermochemical data for halomethanes – NIST¹⁰, Pedley¹¹, JPL¹², Luo¹³, Kurdchaker and Kurdchaker¹⁴, Gurvich et al.¹⁵ - have considerably large error bars or are based on inaccurate experimental information vi) the scarcity of experimental data that is

particularly severe for bromine and iodine containing halomethane species vii) halomethanes such as CH_2Br_2 , CH_2I_2 , CH_2BrI , CH_2ICl , CHClBr_2 and CHCl_2Br and others have been observed in the troposphere, and consequently have been considered important sources of reactive halogens in the atmosphere.¹⁶⁻¹⁹ In this context, quantum mechanical calculations of thermochemical properties of halogenated organic compounds is of importance. Models using methodologies such as isodesmic reaction schemes and/or atomization and quantum chemical calculations are widely applied in predicting thermochemical values. The ab initio Gaussian-n (Gn)²⁰⁻²², Weizman-n²³, and Petersson-style²⁴ complete basis set models have improved accuracy in ab initio thermochemistry by combining calculations at different levels of theory and basis sets with empirical corrections in most methods. The empirical corrections limit their predictive capability to the datasets against which they are benchmarked²⁵. Furthermore, Gn methods are available for chlorine and bromine, but not for iodine.

The present work has the following objectives:

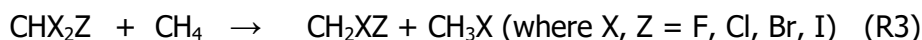
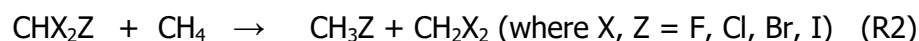
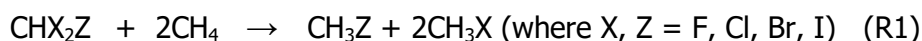
- i) to reproduce the best experimental available values for the standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ of a set of halomethanes by means of isodesmic reactions using ab initio calculations and the DFT, MP2 and CCSD(T) methods
- ii) to obtain the corresponding correlation equations by plotting experimental versus theoretical values of $(\Delta H_f^\circ)_{m(g)}$ for the halomethanes in (i)
- iii) to evaluate the standard molar enthalpy of formation $(\Delta H_f^\circ)_{m(g)}$ of halomethanes where experimental data are either not available – iodine containing or mixed halomethanes - or inconsistent and/or error bars are large ($> 10 \text{ kJ mol}^{-1}$) using the theoretical calculations in (i) and the corresponding correlation equations in (ii)
- iv) To determine the accuracy of the proposed method for predicting standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ of halomethanes
- v) to provide existing databases of thermochemical properties with new and more reliable standard molar enthalpies of formation of these species

The set of the studied halomethanes are shown in Table 1A & 1B. Several of these species and their breakdown products contribute to ozone destruction in both the troposphere and stratosphere²⁶. Mixed trihalomethanes (CHBrCl_2 , CHClBr_2) are also major organic by-products of drinking water chlorination, resulting from the reaction of chlorine with natural organic material and bromine in source waters. The discovery of these by-products in drinking water has raised questions about their toxicity²⁷.

COMPUTATIONAL METHODS

The ab initio molecular orbital calculations were carried out using the Firefly Quantum

Chemistry Package version 8.2.0²⁸⁻²⁹, the GAMESS US program^{29,30} and the ORCA 4.1 quantum chemistry program package³¹. Optimization and frequency calculations of the compounds studied have been carried out with several methods, such as density functional theory (DFT) with the B3LYP³¹ functional and the ADZP basis set³²⁻³⁴, MP2, CCSD(T)³⁵ and DLPNO-CCSD(T)³⁶⁻³⁷ and the SPK-ATZP basis set.³⁸⁻³⁹ Zero-point energies and corrections to enthalpies at 298.15 were added from geometries and frequencies at the level of the geometry optimization. Isodesmic reactions (R1-R3) were used for the calculation of standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ since these has been shown to be more accurate than atomization reactions⁴⁰⁻⁴² due to the cancellation of errors involving similar chemical bonds:



Throughout this paper, standard molar enthalpies of formation and reaction are given in $\text{kJ}\cdot\text{mol}^{-1}$ at a temperature of 298.15 K.

RESULTS AND DISCUSSION

The available experimental values of standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ for the set of halomethanes studied in this work are summarized in Table 1A & 1B. Values of $(\Delta H_f^\circ)_{m(g)}$ collected in reviews and evaluations and from the Argonne Thermochemical Network⁴³ are also included.

As shown, there is poor agreement between experimental $(\Delta H_f^\circ)_{m(g)}$ values in several species. The following experimental values are reported for CHBr_3 (Table 1A & 1B): 55.1 ± 4.9 ⁴⁴, 55.4 ± 3.3 ⁴⁵, 23.8 ± 4.5 ¹¹ $\text{kJ}\cdot\text{mol}^{-1}$. Similarly, the experimental enthalpy of formation values of CH_2BrCl differ considerably -44.1 ± 1.9 ⁴⁶ and -20 ± 7 ¹⁰, -45.0 ± 5 ¹⁵.

The $(\Delta H_f^\circ)_{m(g)}$ values reported for iodine-containing halomethanes (Table 1A) have large error margins. The value reported for CHCl_2I by Gurvich et al.¹⁵ is $5.0 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$ while for CHBr_2I is $110.0 \pm 25 \text{ kJ}\cdot\text{mol}^{-1}$.

The standard molar enthalpies of formation of mixed trihalomethanes are much less well established. Experimental⁴⁴ and computed values⁴⁷ of only two species CHBr_2Cl and CHCl_2Br have been recently determined which is surprising considering the importance of these molecules in atmospheric chemistry.

Computed values $(\Delta H_f^\circ)_{m(g)}$ of the studied compounds using the methods described above and isodesmic reactions (R1-R3) are collected in Table 1A and 1B. As shown, the mean absolute error (MAE) between experimental and computed values of the species

TABLE 1A: $(\Delta H_f^\circ)_m(g)$ values of halomethanes, experimental and computed at DFT/SPK-ATZP and MP2/SPK-ATZP levels of theory.

$(\Delta H_f^\circ)_m(g)$ kJ.mol ⁻¹ (298.15 K)									
Species	DFT/SPK-ATZP			MP2/SPK-ATZP			Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}			
1	CHBr ₃	61.4 (-13.3)	59.0 (-10.9)	43.6 (4.5)	46.4 (1.7)		48.10 [1.3]^f , 55.1 [4.9] ^d , 55.4 [3.3] ^e , 23.8 [4.5] ^g	47.4 ± 2.6	0.7
2	CH ₃ Br	-39.8 (2.1)	-41.6 (3.9)	-33.9 (-3.8)	-29.0 (-8.7)		-37.7 [1.5]^h , -35.4 [1.1] ^g , -35.76 ^f , -38.1 [1.3] ⁱ	-35.5 ± 6.3	-2.2
3	CH ₂ Br ₂	-0.8 (4)	-0.7 (3.9)	0.4 (2.8)	11.9 (-8.7)		3.2 [3.4]^k , 3.5 ^f , 10.0 [15] ^j	3.6 ± 6.5	-0.4
4	CHCl ₃	-87.2 (-15.7)	-93.5 (-9.4)	-99.6 (-3.3)	-102.4 (-0.5)		-102.9 [2.5]^m , -103.2 ⁿ , -103.39 ^f	-98.0 ± 4.6	-4.9
5	CH ₃ Cl	-87.1 (5.2)	-91.3 (9.4)	-83.0 (1.1)	-82.4 (0.5)		-81.9 [1.5]^m , -81.9 [0.5] ^k , - 82.18 ^f	-82.9 ± 0.4	1.0
6	CH ₂ Cl ₂		-105.1 (9.6)		-96.2 (0.5)		-95.7 [1.3]^{g, k} , -95.1 [2.5] ^{m, n} , -95.4 [1.1] ^g	-96.6 ± 0.5	0.9
7	CH ₂ BrCl	-42.0 (-2.1)	-45.1 (1.0)	-45.8 (1.7)	-47.2 (3.1)	-45.8 (1.7)	-44.1 [1.9]^k , -20 [7] ^m , -43.3 ^f , -45.0 [5] ^j	-45.9 ± 0.9	1.8

$(\Delta H_f^\circ)_m(g) \text{ kJ.mol}^{-1} (298.15 \text{ K})$										
	Species	DFT/SPK-ATZP			MP2/SPK-ATZP			Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
		R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}			
8	CHCl ₂ F	-273.5 (-9.8)	-279.8 (-3.5)	-279.8 (-3.5)	-279.6 (-3.7)	-282.4 (-0.9)	-282.4 (-0.9)	-283.3 [13]^{p, q} -284.20 ^f , -284.1 ^r	-282.8 ± 1.2	-0.5
9	CHCl ₂ Br	-37.9 (-12.2)	-44.2 (-5.9)	-44.2 (-5.9)	-51.1 (1.0)	-53.8 (3.7)	-49.3 (-0.8)	-50.1 [1.8]^d , -50.3 ^f , -50.9 [2.4] ^{xo}	-48.2 ± 3.2	-1.9
10	CHBr ₂ Cl	11.6 (-11.6)	9.3 (-9.3)	9.5 (-9.5)	-3.3 (3.3)	-0.5 (0.5)	-1.6 (1.6)	0.0 [3.4]^{lf} , 4.1 ^d , 10.0 ⁱ	-0.8 ± 1.0	0.8
11	CFCI ₃				-283.7 (-5.0)	-287.9 (-0.8)	-287.4 (-1.3)	-288.7 [6.3]^p , -290.1 ^f , -278 ^s	-287.7 ± 1.3	-1
12	CF ₃ Br					-647.9 (-1.0)	-651.6 (2.7)	-648.9 [2.9]^p , -647.0 ^t , -651.57 ^f	-648.3 ± 5.0	-0.6
13	CF ₂ Cl ₂				-485.5 (-6.1)	-488.2 (-3.4)	-489.1 (-2.5)	-491.6 [8]^q , -495.46 ^f , -477.6 ⁱ	-491.5 ± 1.2	-0.1
14	CHF ₂ Cl	-469.2 (-12.4)	-478.0 (-3.6)	-470.7 (-10.9)	-475.4 (-6.2)	-480.1 (-1.5)	-476.4 (-5.2)	-481.6 [13]^q , -482.3 ^u , -482.60 ^f	-480.1 ± 3.4	-1.5
15	CH ₂ CIF	-260.4 (-1.5)	-263.6 (1.7)		-261.0 (-0.9)	-262.4 (0.5)		-261.9 [13]^q , -263.60 ^f	-264.3 ± 1.9	2.4
16	CF ₃ Cl				-697.6 (-12.4)	-704.7 (-5.3)	-708.3 (-1.7)	-710.0 [3.3]^q , -710.08 ^f , -707.3 ^w	-708.9 ± 3.5	-1.1

$(\Delta H_f^\circ)_m(\text{g}) \text{ kJ.mol}^{-1} (298.15 \text{ K})$										
Species		DFT/SPK-ATZP			MP2/SPK-ATZP			Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
		R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}			
17	CH₂ICI	8.0 (2.7)	8.9 (1.8)	8.0 (2.7)	11.3 (-0.6)	9.9 (0.8)		10.7 [1.9]^k , 13.6 ^v	9.6 ± 2.9	1.1
18	CH₂IBr	59.0 (-4.0)	59.8 (-4.8)		56.0 (-1.0)	55.7 (-0.7)		55.0 [3.4]^k , 57.1 ^v	58.0 ± 2.3	-3.0
19	CHI₂Cl	112.9 (-2.9)	114.6 (-4.6)		110.6 (-0.6)	109.2 (0.8)	110.0 (0)	110.0 [30]^l , 112.9 ^v	113.5 ± 2.3	-3.5
20	CHI₂Br	168.9 (-3.9)	167.7 (-2.7)		155.1 (9.9)	163.5 (1.5)		165.0 [35]^l , 158.20 ^v	165.4 ± 4.7	-0.4
21	CHCl₂I	7.2 (-2.2)	0.9 (4.1)	9.9 (-4.9)	7.7 (-2.7)	4.9 (0.1)	7.1 (-2.1)	5.0 [20]^l , 8.28 ^v	7.0 ± 2.3	-2.0
22	CHBr₂I	113.2 (-3.2)	110.9 (-0.9)	109.3 (0.7)	100.0 (10.0)	104.2 (5.8)	99.0 (11.0)	110.0 [25]^l , 93.51 ^v	105.6 ± 4.0	4.4
23	CF₂ClI	-376.6 (-3.4)	-382.7 (2.7)	-389.0 (9)	-366.0 (-14.0)	-371.3 (-8.7)	-372.2 (-7.8)	-380.0 [25]^l , .379.07 ^v	-372.3 ± 1.3	-7.7
24	CF₂BrI	-320.9 (-4.1)	-327.0 (2)	-327.8 (2.8)	-316.1 (-8.9)	-317.8 (-7.2)	-318.4 (-6.6)	-325.0 [25]^l , -324.30 ^v	-325.1 ± 6.0	0.1
25	CFCl₂I	-175.3 (-4.7)	-181.9 (1.9)	-177.5 (-2.5)	-169.9 (-10.1)	-174.9 (-5.1)	-173.5 (-6.5)	-180.0 [20]^l , .178.20 ^v	-176.3 ± 3.3	-3.7
26	CFI₂Cl	-70.1 (0.1)	-69.8 (-0.2)	-71.6 (1.6)	-57.9 (-12.1)	-50.4 (-19.6)	-58.8 (-11.2)	-70 [30]^l , -79.49 ^v	-60.5 ± 7.4	-9.5
27	CFBr₂I		-71.3 (1.3)		-68.6 (-1.4)	-84.1 (14.1)	-72.9 (2.9)	-70 [25]^l , .79.41 ^v	-72.3 ± 7.2	2.3

$(\Delta H_f^\circ)_m(g)$ kJ.mol ⁻¹ (298.15 K)									
Species	DFT/SPK-ATZP			MP2/SPK-ATZP			Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}			
Mean Abs. Error ^{x1} (MAE)	(5.8)	(4.3)	(4.5)	(5.1)	(3.9)	(4.1)	[11.8]	[3.2]	(2.2)
Mean Abs. Error (corr.) (MAEC)	(5.8)	(4.3)	(4.5)	(3.9) ^{x2}	(2.8) ^{x2}	(3.0) ^{x2}	[9.5] ^{x2}	[3.0] ^{x2}	(1.7) ^{x2}
rms error ^{x3}	7.9	5.8	5.7	5.1	4.5	4.1	16.1	3.6	2.1
Mean Signed Error from (EX) ^{x4} (MSE)	-4.4	-0.5	-1.5	-2.3	-1.4	-1.3			-0.3

^a R1, R2, R3 refer to reactions (1), (2) and (3) ^b Values in brackets represent reported experimental uncertainties of $(\Delta H_f^\circ)_m(g)$. The listed uncertainties of evaluations correspond to estimated 95% confidence limits as customary in thermochemistry. The most reliable values of $(\Delta H_f^\circ)_m(g)$ are written in bold. ^c Values in parentheses represent errors (deviations) from experimental data $[(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}]$. ^d From ref. 44, ^e From ref. 45, ^f From ref. 43, ^g From ref. 11, ^h From ref. 49, ⁱ From ref. 50, ^k From ref. 46, ^j From ref. 15, ^m From ref. 10, ⁿ From ref. 51, ^o From ref. 52, ^p From ref. 53, ^q From ref. 54, ^r From ref. 55, ^s From ref. 56, ^t From ref. 57, ^u From ref. 58, ^v From ref. 14 (according to the authors the estimated error is less than ± 8.4 kJ. mol⁻¹ except in compounds containing ClI and BrI bonds where it may be as high as ± 20.9 kJ. mol⁻¹), ^w From ref. 59, ^x Evaluations from ref. 47 ^{x1} Mean Absolute Error $|(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}|$ ^{x2} Mean Absolute Error $|(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}|$ excluding samples, #23, #24, #25, #26. ^{x3} rms error of $(\Delta H_f^\circ)_m(g)$ excluding samples #25, #26, #27, #28. ^{x4} Mean Signed Error $[(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}]$.

TABLE 1B: $(\Delta H_f^\circ)_m(g)$ values of halomethanes, experimental and computed at CCSD(T)/SPK-ATZP level of theory.

$(\Delta H_f^\circ)_m(g)$ kJ.mol ⁻¹ (298.15 K)							
Species		CCSD(T)/SPK-ATZP					
		R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
1	CHBr ₃	51.0 (-2.9)	47.5 (0.6)		48.10 [1.3]^f , 55.1 [4.9] ^d , 55.4 [3.3] ^e , 23.8 [4.5] ^g	47.4 ± 2.6	0.7
2	CH ₃ Br	-35.2 (-2.5)	-31.9 (-5.8)		-37.7 [1.5]^h , -35.4 [1.1] ^g , -35.76 ^f , -38.1 [1.3] ⁱ	-35.5 ±6.3	-2.2
3	CH ₂ Br ₂	1.4 (1.8)	9.0 (-5.8)		3.2 [3.4]^k , 3.5 ^f , 10.0 [15] ^j	3.6 ± 6.5	-0.4

$(\Delta H_f^\circ)_m(g)$ kJ.mol ⁻¹ (298.15 K)						
Species	CCSD(T)/SPK-ATZP					
	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
4 CHCl₃	-99.0 (-3.9)	-101.7 (-1.2)		-102.9 [2.5]^m -103.2 ⁿ , -103.39 ^f	-98.0 ± 4.6	-4.9
5 CH₃Cl	-83.2 (1.3)	-83.1 (1.2)		-81.9 [1.5]^m -81.9 [0.5] ^k , -82.18 ^f	-82.9 ± 0.4	1.0
6 CH₂Cl₂		-96.9 (1.2)		-95.7 [1.3]^{g, k} -95.1 [2.5] ^{m, n} , -95.4 [1.1] ^g	-96.6 ± 0.5	0.9
7 CH₂BrCl	-44.9 (0.8)	-46.3 (2.2)		-44.1 [1.9]^k , -20 [7] ^m , -43.3 ^f , -45.0 [5] ⁱ	-45.9 ± 0.9	1.8
8 CHCl₂F		-283.2 (-0.1)	-279.6 (-3.7)	-283.3 [13]^{p, q} -284.20 ^f , -284.1 ^r	-282.8 ± 1.2	-0.5
9 CHCl₂Br	-49.5 (-0.6)	-52.2 (2.1)	-48.7 (-1.4)	-50.1 [1.8]^d , -50.3 ^f , -50.9 [2.4] ^{xo}	-48.2 ± 3.2	-1.9
10 CHBr₂Cl	-0.6 (0.6)	1.1 (-1.1)	0.1 (-0.1)	0.0 [3.4]^{l, f} , 4.1 ^d , 10.0 ⁱ	-0.8 ± 1.0	0.8
11 CFCI₃	-286.7 (-2.0)	-287.8 (-0.9)	-289.4 (0.7)	-288.7 [6.3]^p , -290.1 ^f , -278 ^s	-287.7 ± 1.3	-1
12 CF₃Br	-649.9 (1.0)	-649.0 (0.1)	-654.4 (5.5)	-648.9 [2.9]^p , -647.0 ^t , -651.57 ^f	-648.3 ± 5.0	-0.6
13 CF₂Cl₂	-492.4 (0.8)	-495.1 (3.5)	-495.2 (3.6)	-491.6 [8]^q -495.46 ^f , -477.6 ⁱ	-491.5 ± 1.2	-0.1
14 CHF₂Cl	-480.8 (-0.8)	-483.3 (1.7)	-479.9 (-1.7)	-481.6 [13]^q , -482.3 ^u , -482.60 ^f	-480.1 ± 3.4	-1.5
15 CH₂CIF	-263.3 (1.4)	-264.2 (2.3)		-261.9 [13]^q , -263.60 ^f	-264.3 ± 1.9	2.4
16 CF₃Cl	-707.1 (-2.9)	-710.9 (0.9)	-711.6 (1.6)	-710.0 [3.3]^q -710.08 ^f , -707.3 ^w	-708.9 ± 3.5	-1.1
17 CH₂ICl	12.0 (-1.3)	10.6 (0.1)		10.7 [1.9]^k , 13.6 ^v	9.6 ± 2.9	1.1
18 CH₂IBr	57.4 (-2.4)	55.7 (-0.7)		55.0 [3.4]^k , 57.1 ^v	58.0 ± 2.3	-3.0

$(\Delta H_f^\circ)_m(g)$ kJ.mol ⁻¹ (298.15 K)						
Species	CCSD(T)/SPK-ATZP					
	R1 ^{a, c}	R2 ^{a, c}	R3 ^{a, c}	Experim. (EX) ^b	Eval. (EV) ^b	EX-EV
19 CHI₂Cl	114.7 (-4.7)	113.3 (-3.3)		110.0 [30] ^f , 112.9 ^v	113.5 ± 2.3	-3.5
20 CHI₂Br	160.6 (4.4)	167.0 (-2.0)		165.0 [35] ^f , 158.20 ^v	165.4 ± 4.7	-0.4
21 CHCl₂I	9.8 (-4.8)	7.1 (-2.1)	7.9 (-2.9)	5.0 [20] ^f , 8.28 ^v	7.0 ± 2.3	-2.0
22 CHBr₂I	104.0 (6.0)	107.2 (2.8)	101.6 (8.4)	110.0 [25] ^f , 93.51 ^v	105.6 ± 4.0	4.4
23 CF₂ClI	-375.8 (-4.2)	-379.7 (-0.3)	-377.0 (-3.0)	-380.0 [25] ^f , -379.07 ^v	-372.3 ± 1.3	-7.7
24 CF₂BrI				-325.0 [25] ^f , -324.30 ^v	-325.1 ± 6.0	0.1
25 CFCl₂I	-173.7 (-6.3)	-179.6 (-0.4)	-178.3 (-1.7)	-180.0 [20] ^f , -178.20 ^v	-176.3 ± 3.3	-3.7
26 CFI₂Cl	-59.8 (-10.2)	-52.5 (-17.5)	-59.0 (-11.0)	-70 [30] ^f , -79.49 ^v	-60.5 ± 7.4	-9.5
27 CFBr₂I	-69.8 (-0.2)	-81.8 (11.8)	-64.3 (-5.7)	-70 [25] ^f , -79.41 ^v	-72.3 ± 7.2	2.3
Mean Abs. Error^{x1} (MAE)	(2.8)	(2.8)	(3.6)		[3.2]	(2.2)
Mean Abs. Error (corr.) (MAEC)	(2.2)^{x2}	(2.3)^{x2}	(3.2)^{x2}		[3.0]^{x2}	(1.7)^{x2}
rms error^{x3}	2.8	3.4	4.0		3.6	2.1
Mean Signed Error from (EX)^{x4} (MSE)	-1.3	-0.4	-0.8			-0.3

^a R1, R2, R3 refer to reactions (1), (2) and (3). ^b Values in brackets represent reported experimental uncertainties of $(\Delta H_f^\circ)_m(g)$. The listed uncertainties of evaluations correspond to estimated 95% confidence limits as customary in thermochemistry. The most reliable values of $(\Delta H_f^\circ)_m(g)$ are written in bold. ^c Values in parentheses represent errors (deviations) from experimental data $(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}$. ^d From ref. 44, ^e From ref. 45, ^f From ref. 43, ^g From ref. 11, ^h From ref. 49, ⁱ From ref. 50, ^k From ref. 46, ^l From ref. 15, ^m From ref. 10, ⁿ From ref. 51, ^o From ref. 52, ^p From ref. 53, ^q From ref. 54, ^r From ref. 55, ^s From ref. 56, ^t From ref. 57, ^u From ref. 58, ^v From ref. 14 (according to the authors the estimated error is less than ±8.4 kJ. mol⁻¹ except in compounds containing ClI and BrI bonds where it may be as high as ±20.9 kJ. mol⁻¹), ^w From ref. 59, ^x Evaluations from ref. 47 ^{x1} Mean Absolute Error $|(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}|$. ^{x2} Mean Absolute Error $|(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}|$ excluding samples #23, #24, #25, #26. ^{x3} rms error $(\Delta H_f^\circ)_m(g)$ excluding samples #25, #26, #27, #28. ^{x4} Mean Signed Error $[(\Delta H_f^\circ)_m(g)_{\text{experimental}} - (\Delta H_f^\circ)_m(g)_{\text{computed}}]$.

studied $|(\Delta H_f^\circ)_{m(g)\text{experimental}} - (\Delta H_f^\circ)_{m(g)\text{computed}}|$ is near or below 4.5 kJ.mol^{-1} . This value is very similar to the mean absolute deviation of $\sim 4.184 \text{ kJ.mol}^{-1}$ accuracy found for a large number of molecules with reliable experimental standard molar enthalpies of formation. Exceptions are observed at the DFT and MP2 level when reaction R1 was used (MAE = 5.8 and 5.1 respectively, Table 1A).

Computations at the DFT level which are computationally inexpensive gave MAE values that range from 4.3 to 5.8 kJ.mol^{-1} . Computations at the MP2 level gave MAE values that range from 4.1 to 5.1 kJ.mol^{-1} while those at the CCSD(T) level range from 2.8 to 3.6 kJ.mol^{-1} (Table 1A & 1B). Deviations (MAE) between experimental and computed values decrease if the iodine containing mixed halomethanes CF_2ClI , CF_2BrI , CFCl_2I and CFI_2Cl are excluded since they tend to rise with increasing halogen substitution.⁵⁴ In such a case,

when the above halomethanes are excluded MAE of the compounds studied ranges from 2.8 to 3.9 kJ.mol^{-1} at the MP2 and from 2.2 to 3.2 kJ.mol^{-1} at the CCSD(T) level respectively while it remains unaffected at the DFT level (Table 1A & 1B).

Furthermore, the small mean signed errors (MSE) between experimental and computed values ranging from -0.4 to -2.3 kJ.mol^{-1} (except at the DFT level when reaction R1 was used, MSE = -4.4) show that the computed standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ as an average lie in most cases slightly higher than the corresponding reported experimental values (Table 1A & 1B).

The rms errors of computed values using the DFT, MP2 and CCSD(T) methods range from 2.8 to 5.8 kJ.mol^{-1} (except at the DFT level when reaction R1 was used, rms error = 7.9) which are well below the rms experimental uncertainty of 16.1 kJ.mol^{-1} (Table 1A & 1B).

Plots of $(\Delta H_f^\circ)_{m(g)\text{experimental}}$ versus $(\Delta H_f^\circ)_{m(g)\text{computed}}$ values using reactions (R1)-(R3) at the DFT, MP2 and CCSD(T) levels of theory show excellent correlation and the following best-fitted linear equations and R^2 values are obtained:

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0210 * (\Delta H_f^\circ)_{m(\text{DFT, reaction R1})} - 2.9580; \quad R^2 = 0.9990 \quad (1)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0114 * (\Delta H_f^\circ)_{m(\text{DFT, reaction R2})} + 0.4942; \quad R^2 = 0.9989 \quad (2)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 0.9998 * (\Delta H_f^\circ)_{m(\text{DFT, reaction R3})} - 1.1264; \quad R^2 = 0.9996 \quad (3)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0227 * (\Delta H_f^\circ)_{m(\text{MP2, reaction R1})} + 1.7667; \quad R^2 = 0.9996 \quad (4)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0053 * (\Delta H_f^\circ)_{m(\text{MP2, reaction R2})} + 0.4192; \quad R^2 = 0.9994 \quad (5)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0069 * (\Delta H_f^\circ)_{m(\text{MP2, reaction R3})} + 0.5835; \quad R^2 = 0.9996 \quad (6)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0018 * (\Delta H_f^\circ)_{m(\text{CCSD(T), reaction R1})} + 0.5885; \quad R^2 = 0.9991 \quad (7)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 0.9948 * (\Delta H_f^\circ)_{m(\text{CCSD(T), reaction R3})} - 0.8595; \quad R^2 = 0.9995 \quad (9)$$

The $(\Delta H_f^\circ)_{m(g)}$ average value of CHBr_2Cl was found to be $-0.8 \pm 1.0 \text{ kJ.mol}^{-1}$ in excellent agreement with the value reported by the Argonne Thermochemical Network⁴³ $0.0 \pm 3.4 \text{ kJ.mol}^{-1}$. The experimental value reported by Shuman et al.⁴⁴ was $4.1 \pm 4.9 \text{ kJ.mol}^{-1}$. The standard molar enthalpy of formation of CHBr_2Cl has also been estimated by Gurvich et al.¹⁵ to be 10 kJ.mol^{-1} , at 298 K, however with uncertainty greater than 10 kJ.mol^{-1} .

Similarly, the reliable $(\Delta H_f^\circ)_{m(g)}$ average value of CHCl_2Br was found to be $-48.2 \pm 3.2 \text{ kJ.mol}^{-1}$ in the limits of the estimated uncertainty of the experimental value reported by Shuman et al.⁴⁴ $-50.1 \pm 1.8 \text{ kJ.mol}^{-1}$. The estimated value reported by Davalos et al.⁴⁷ was $-50.9 \pm 2.4 \text{ kJ.mol}^{-1}$ and by the Argonne Thermochemical Network⁴³ $-50.3 \pm 1.3 \text{ kJ.mol}^{-1}$.

The reliable $(\Delta H_f^\circ)_{m(g)}$ average values of the environmentally important CHCl_2Br and CHBr_2Cl were evaluated as described above. Both species have been considered important sources of reactive halogens in the atmosphere and reliable $(\Delta H_f^\circ)_{m(g)}$ experimental data⁴⁶ were not available until recently.

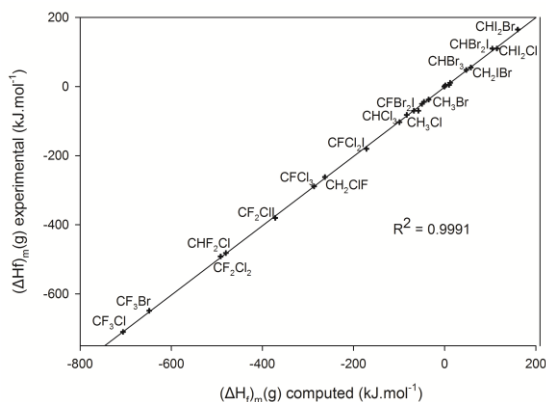


Figure 3. $(\Delta H_f^o)_m(g)$ of halomethane molecules in Table 1B obtained at the CCSD(T) level of theory and SPK-ATZP basis set using reaction R1 vs. their corresponding experimental values.

The reliable $(\Delta H_f^o)_m(g)$ average value of CH_2BrCl was also determined in this study and found to be equal to $-45.9 \pm 0.9 \text{ kJ.mol}^{-1}$ which is in agreement within the estimated uncertainty with the experimental value reported by Lago et al.⁴⁶ $-44.1 \pm 1.9 \text{ kJ.mol}^{-1}$. The value reported by the Argonne Thermochemical Network43 is $-43.3 \pm 1.4 \text{ kJ.mol}^{-1}$.

The $(\Delta H_f^o)_m(g)$ average values of a series of chlorofluoromethanes and one bromofluoromethane (CHCl_2F , CFCl_3 , CF_2Cl_2 , CHF_2Cl , CH_2ClF , CF_3Cl , CF_3Br) were evaluated and found in close agreement with the corresponding experimental literature values (Table 1A & 1B). The $[(\Delta H_f^o)_m(g)_{\text{experimental}} - (\Delta H_f^o)_m(g)_{\text{evaluated}}]$ standard molar enthalpy of formation differences lie between $-1.5 - 2.4 \text{ kJ.mol}^{-1}$.

The $(\Delta H_f^o)_m(g)$ average values of the iodine containing dihalomethanes CH_2ICl and CH_2IBr were also estimated and found to be $9.6 \pm 2.9 \text{ kJ.mol}^{-1}$ and $58.0 \pm 2.3 \text{ kJ.mol}^{-1}$ respectively (Table 1A & 1B). The corresponding experimental values⁴⁶ $10.7 \pm 1.9 \text{ kJ.mol}^{-1}$ and $55.0 \pm 3.4 \text{ kJ.mol}^{-1}$ are in agreement with the above results within the reported experimental error. The above experimental values and the reported evaluations correct the old literature values and reduce their uncertainties (old literature $(\Delta H_f^o)_m(g)$ values of CH_2ICl : $13.6 \pm 20 \text{ kJ.mol}^{-1}$

by Kudchadker et al.¹⁴, $5 \pm 25 \text{ kJ.mol}^{-1}$ by Skorobogatov et al.⁴⁸ and of CH_2IBr : $57.1 \pm 20 \text{ kJ.mol}^{-1}$ by Kudchadker et al.¹⁴).

The absolute errors with respect to experimental standard molar enthalpies of formation $|(\Delta H_f^o)_m(g)_{\text{experimental}} - (\Delta H_f^o)_m(g)_{\text{computed}}|$ of molecules #1-#16 (Table 1A & 1B, column EX-EV) were found to be lower than 2.4 kJ.mol^{-1} (exception CHCl_3 , absolute error: 4.9 kJ.mol^{-1}). These values are below of the mean absolute deviation of $\sim 4.184 \text{ kJ.mol}^{-1}$ accuracy found for a large number of molecules with reliable experimental standard molar enthalpies of formation. The present results on halomethanes provide evidence that our approach is generally capable of predicting standard molar enthalpies of formation near to chemical accuracy.

Since these results support the reliability of our calculations the study was extended to the standard molar enthalpies of formation of mixed iodomethanes which are much less well established. Reliable experimental values could be found for only two compounds CH_2ICl and CH_2IBr described above – but several of them have been estimated by Gurvish et al. with uncertainties greater than 10 kJ.mol^{-1} (Table 1A & 1B).

The $(\Delta H_f^o)_m(g)$ average values (kJ.mol^{-1}) of CHI_2Cl , CHI_2Br , CHCl_2I and CHBr_2I determined in this study 113.5 ± 2.3 (110.0 ± 30), 165.4 ± 4.7 (165.0 ± 35), 7.0 ± 2.3 (5.0 ± 20), 105.6 ± 4.0 (110.0 ± 25) respectively, are in agreement within the estimated uncertainty with the values reported in literature by Gurvish et al.¹⁵ (values in parentheses above and in Table 1A & 1B). They are also in agreement with the corresponding values 112.90 , 158.20 , 8.28 and $93.51 \text{ kJ.mol}^{-1}$ reported by Kudchadker et al.¹⁴ with an uncertainty as high as 20.9 kJ.mol^{-1} . However the large uncertainty in the literature values makes it difficult to draw any definitive conclusion regarding the accuracy of the method as it occurred for CH_2ICl and CH_2IBr where calculated values were within the

reported narrow experimental errors. For these molecules additional theoretical studies are needed with high-accuracy calculations.

The present study was further extended to mixed halomethanes that are completely substituted with halogen atoms such as CF₂ClI, CF₂BrI, CFCl₂I, CFI₂Cl and CFBr₂I. The reliable $(\Delta H_f^\circ)_{m(g)}$ average values (kJ.mol⁻¹) of the above compounds determined in this study - 372.3 ± 1.3 (-380.0 ± 25), -325.1 ± 6.0 (-325.0 ± 25), -176.3 ± 3.3 (-180.0 ± 20), -60.5 ± 7.4 (-70 ± 30) and -72.3 ± 7.2 (-70 ± 25) respectively are in agreement within the estimated uncertainty with the values reported in literature by Gurvish et al.¹⁵ (values in parentheses above and in Table 1A & 1B). It is evident from the comparison of the calculated and experimental $(\Delta H_f^\circ)_{m(g)}$ values of the mixed halomethanes that the calculated value of CF₂BrI -325.1 ± 6.0 kJ.mol⁻¹ coincides with the value reported by Gurvish et al.¹⁵ -325.0 ± 25.0 kJ.mol⁻¹ and is in good agreement with the value reported by Kudchadker et al.¹⁴ 324.30 kJ.mol⁻¹ (Table 1A & 1B). The calculated value of CFCl₂I -176.3 ± 3.3 kJ.mol⁻¹ is closer to the value reported by Kudchadker et al.¹⁴ 178.2 kJ.mol⁻¹ (Table 1A & 1B) compared to the value reported by Gurvish et al.¹⁵ -180.0 ± 20 kJ.mol⁻¹. However, as mentioned above the large uncertainty in the literature values (20-30 kJ.mol⁻¹) makes it difficult to draw any definitive conclusion regarding the accuracy of the method.

The absolute errors with respect to the experimental standard molar enthalpies of formation $|(\Delta H_f^\circ)_{m(g)\text{experimental}} - (\Delta H_f^\circ)_{m(g)\text{evaluated}}|$ of the mixed halomethane molecules #19-#27 (Table 1A & 1B, column EX-EV) were found to be lower than 4.5 kJ.mol⁻¹ (exception CF₂ClI, absolute error: 7.7 kJ.mol⁻¹ and CFI₂Cl absolute error: 9.5 kJ.mol⁻¹) (Table 2).

The average of standard molar enthalpy of formation difference $|(\Delta H_f^\circ)_{m(g)\text{experimental}} - (\Delta H_f^\circ)_{m(g)\text{evaluated}}|$ of these compounds was equal to 3.7 kJ.mol⁻¹ while the rms of $[(\Delta H_f^\circ)_{m(g)\text{experimental}} - (\Delta H_f^\circ)_{m(g)\text{evaluated}}]$ was found to be equal to 4.8 kJ.mol⁻¹ that is well below the rms uncertainty of the experimental results (literature values) of 26.5 kJ.mol⁻¹ (Table 2).

The methodology described above that yielded comparably good agreement with experimental standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ was used to compute standard molar $(\Delta H_f^\circ)_{m(g)}$ of selected radicals and bond dissociation energies (BDE's) of the studied compounds in Table 1A & 1B. These values were derived using reactions (R4 and R5) at the MP2/SPK-ATZP, DFT/BMK/SPK-ATZP and at the CCSD(T)(DLPNO)/SPK-ATZP level (Table 3). Optimization and frequency calculations were carried out at the DFT/BMK/SPK-ATZP and MP2/SPK-ATZP levels of theory. Single-point calculations at the CCSD(T)/SPK-ATZP level were carried out on the MP2/SPK-ATZP optimized geometries.



(where X = F, Cl, Br, I and n= 1, 2, 3..)

The bond dissociation energies (BDE's) of the studied compounds can be evaluated from calculated values of $(\Delta H_f^\circ)_{m(g)}$ for the neutral species (Table 1A & 1B) and their corresponding radicals (Table 3) and the $(\Delta H_f^\circ)_{m(g)}$ values for chlorine (121.301 ± 0.008 kJ.mol⁻¹)¹⁰, bromine (111.87 ± 0.12 kJ.mol⁻¹)¹⁰ and iodine (106.76 ± 0.04 kJ.mol⁻¹)¹⁰

TABLE 2: Average value of the enthalpy difference $|(\Delta H_f^\circ)_{m(g)}|_{diff}$ (kJ.mol⁻¹) between experimental (literature values) and evaluated data of selected mixed halomethanes in Table 1A & 1B [where $|(\Delta H_f^\circ)_{m(g)}|_{diff} = |(\Delta H_f^\circ)_{m(g)}_{experimental} - (\Delta H_f^\circ)_{m(g)}_{evaluated}|$].

Compound # (Table 1A & 1B)	Species	$ (\Delta H_f^\circ)_{m(g)} _{diff}^{a, b}$ (kJ.mol ⁻¹)
19	CHI ₂ Cl	3.5 (30)
20	CHI ₂ Br	0.4 (35)
21	CHCl ₂ I	2.0 (20)
22	CHBr ₂ I	4.4 (25)
23	CF ₂ ClI	7.7 (25)
24	CF ₂ BrI	0.1 (25)
25	CFCl ₂ I	3.7 (20)
26	CFI ₂ Cl	9.5 (30)
27	CFBr ₂ I	2.3 (25)
Average		3.7
rms		4.8 (26.5)

^a $(\Delta H_f^\circ)_{m(g)}$ at 298.15 K in units of kJ.mol⁻¹ ^b Values in parentheses represent reported experimental uncertainties of $(\Delta H_f^\circ)_{m(g)}$ (Table 1A & 1B).

according to the definition of homolytic X-Y bond cleavage enthalpy of reaction at 298.15 K (R6).



The standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ of the radicals illustrated in Figure 4 were computed by the MP2/SPK-ATZP, DFT/BMK/SPK-ATZP and CCSD(T)(DLPNO)/SPK-ATZP methods and show excellent correlation with the experimental values. The corresponding linear equations are (10), (11) and (12) with R² values 0.9990, 0.9972 and 0.9992 respectively.

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0023 * (\Delta H_f^\circ)_{m(\text{MP2/SPK-ATZP, reaction R5})} - 2.6720; \quad R^2 = 0.9990 \quad (10)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0365 * (\Delta H_f^\circ)_{m(\text{DFT/BMK/SPK-ATZP, reaction R5})} + 1.2666; \quad R^2 = 0.9972 \quad (11)$$

$$(\Delta H_f^\circ)_{m(\text{experimental})} = 1.0184 * (\Delta H_f^\circ)_{m(\text{CCSD(T)(DLPNO)/SPK-ATZP, reaction R5})} + 2.1437; \quad R^2 = 0.9992 \quad (12)$$

The best correlations were obtained using the CCSD(T)(DLPNO)/SPK-ATZP and MP2/SPK-ATZP methods.

As shown in Table 3, the mean absolute error (MAE) between experimental and computed values $|(\Delta H_f^\circ)_{m(g)}^{\text{experimental}} - (\Delta H_f^\circ)_{m(g)}^{\text{computed}}|$ of the organic radicals studied was found to be 3.1 and 4.6 kJ.mol⁻¹ when the MP2/SPK-ATZP and CCSD(T)(DLPNO)/SPK-ATZP methods were used respectively. These values are close to the mean absolute deviation (MAE) of experimental standard molar enthalpies of formation of the same radicals that was calculated to be equal to 4.3 kJ.mol⁻¹. The DFT/BMK/SPK-ATZP method (MAE = 6.2, Table 3) exhibited larger deviations from the experimental values.

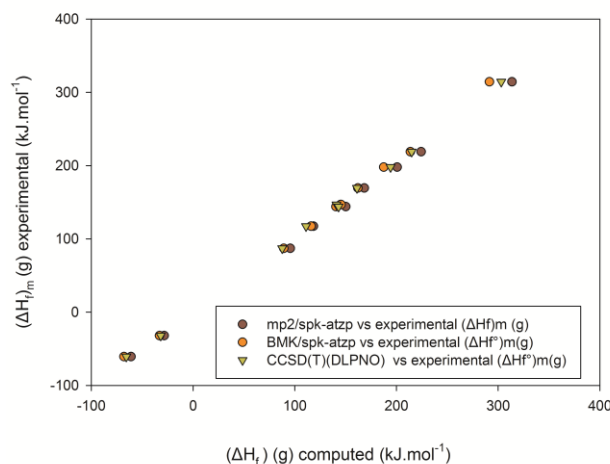


Figure 4. $(\Delta H_f^\circ)_m(g)$ of radicals in Table 3 obtained at the MP2, BMK and CCSD(T)(DLPNO) level of theory and SPK-ATZP basis set using reactions R4 and R5 vs. their corresponding experimental values

The reliable $(\Delta H_f^\circ)_{m(g)}$ average values of the radicals listed in Table 3 were evaluated by extrapolating their computed values, which are obtained in this work, from correlation equations (10) – (12) and reactions R4 and R5. The reported uncertainties of evaluations correspond to estimated 95% confidence limits.

The reliable $(\Delta H_f^\circ)_{m(g)}$ average value of the CH₃ radical was found to be 146.8 ± 0.3 kJ.mol⁻¹ in agreement within the estimated uncertainty with the experimental value reported by Luo¹³ 146.7 ± 0.3 kJ.mol⁻¹ and within twice the experimental uncertainty reported by Ruscic et al.⁶⁰ 145.7 ± 0.8 kJ.mol⁻¹ (Table 3). The reliable $(\Delta H_f^\circ)_{m(g)}$ average value of the CH₂F radical -31.5 ± 3.3 kJ.mol⁻¹ is also in good agreement –within the estimated uncertainty- with the values reported by Pickard et al.⁶¹ and McMillen et al.⁶² -32 ± 8 and -32.6 ± 8.4 kJ.mol⁻¹ respectively. Similarly, the computed $(\Delta H_f^\circ)_{m(g)}$ average values of CH₂Cl 115.5 ± 4.5 kJ.mol⁻¹, CHBr₂ 198.0 ± 5.5 kJ.mol⁻¹, CHClF -65.9 ± 7.0 kJ.mol⁻¹ and CHI₂ 311.2 ± 5.8 kJ.mol⁻¹ agree well within the experimental uncertainty with the values reported by Luo¹³ 117.3 ± 3.1 kJ.mol⁻¹, Davalos et al.⁴⁷ 197.8 ± 4.3 kJ.mol⁻¹, Seetula et al.⁶⁴ -60.7 ± 10 kJ.mol⁻¹ and Seetula et al.⁶⁸ 314.4 ± 3.3 kJ.mol⁻¹ respectively (Table 3).

The reliable $(\Delta H_f^\circ)_{m(g)}$ average values of CH_2Br radical $166.2 \pm 1.3 \text{ kJ.mol}^{-1}$, CH_2I $222.4 \pm 4.0 \text{ kJ.mol}^{-1}$ and CHBrCl $147.8 \pm 0.6 \text{ kJ.mol}^{-1}$ were also evaluated and found to be within twice the experimental uncertainty reported by Davalos et al.⁴⁷ $169.4 \pm 3.0 \text{ kJ.mol}^{-1}$, $215.7 \pm 6.7 \text{ kJ.mol}^{-1}$ and $143.9 \pm 3.7 \text{ kJ.mol}^{-1}$ respectively (Table 3).

As shown in Table 3, the MAE and rms errors of the radical evaluations were found to be equal to 3.6 kJ.mol^{-1} and 4.1 kJ.mol^{-1} respectively. These values are below the corresponding MAE and rms uncertainty of the experimental results (literature values) of 4.3 and 5.2 kJ.mol^{-1} (Table 3).

Since these results support the reliability of our calculations the study was extended to the standard molar enthalpies of formation of CHCl and CHBr . Experimental standard molar enthalpies of formation of these radicals are not available in the literature to the best of our knowledge. The reliable $(\Delta H_f^\circ)_{m(g)}$ average values of CHCl and CHBr radicals computed here using the method described above were found to be $200.1 \pm 4.5 \text{ kJ.mol}^{-1}$ and $249.7 \pm 3.3 \text{ kJ.mol}^{-1}$ respectively.

The bond dissociation energies (BDE's) of the studied compounds were subsequently derived from reaction R6 using the most reliable evaluations of $(\Delta H_f^\circ)_{m(g)}$ for the neutral species (Table 1A & 1B) and their corresponding radicals (Table 3) and the $(\Delta H_f^\circ)_{m(g)}$ values for fluorine (79.36 ± 0.048), chlorine ($121.228 \pm 0.0011 \text{ kJ.mol}^{-1}$)⁴³, bromine ($111.855 \pm 0.056 \text{ kJ.mol}^{-1}$)⁴³ and iodine ($106.757 \pm 0.0021 \text{ kJ.mol}^{-1}$)⁴³. These values are shown in Table 4 where the corresponding BDE's calculated at the MP2/SPK-ATZP and CCSD(T)/SPK-ATZP level are also listed.

The rms error of the evaluated BDE values was found to be equal to 4.9 compared to 8.2 kJ.mol^{-1} of the experimental/literature values (Table 4).

For most of the above BDE evaluations good agreement was observed between calculated and experimental/literature values (deviations less than 4.8 kJ.mol^{-1}). For a few of the iodinated-molecules and for a fluorine containing molecule ($\text{Cl-CH}_2\text{I}$, $\text{I-CH}_2\text{Br}$, $\text{F-CH}_2\text{Cl}$) deviations were found to be around 6.0 kJ.mol^{-1} . The largest difference was observed for Br-CHBr_2 (12.4 kJ.mol^{-1} , in agreement with the difference reported by S.W. North et al.⁷⁰ 12.6 kJ.mol^{-1} at the MP2 and CCSD(T) levels of theory), Cl-CHClBr (-9.2 kJ.mol^{-1}) and Cl-CHFCl (7.9 kJ.mol^{-1}). However, the BDE values reported for the above species in this paper are within experimental error with the literature values where large associated uncertainties were observed 13.0 , 17.0 and 13.4 kJ.mol^{-1} respectively. The estimated BDE values reported for Br-CHBr_2 and Cl-CHClBr by Davalos et al.⁴⁷ $254.3 \pm 5.4 \text{ kJ.mol}^{-1}$ and $316.1 \pm 4.4 \text{ kJ.mol}^{-1}$ respectively are in better agreement to the ones reported in this work (Table 4). Only for five of the iodinated-molecules in Table 4 experimental/literature BDE(C-X) values are available to the best of our knowledge. The BDE(C-X) values reported in this study for $\text{Cl-CH}_2\text{I}$, $\text{Br-CH}_2\text{I}$, $\text{I-CH}_2\text{Cl}$ and $\text{I-CH}_2\text{I}$ are in agreement within the estimated uncertainty with the experimental values reported in literature. The BDE value of $\text{I-CH}_2\text{Br}$ evaluated and reported in Table 4 was found to be

within twice the experimental uncertainty of the value estimated and reported by Davalos et al.⁴⁷ but within the experimental uncertainty of the value determined by Lago⁴⁶. For the rest of the iodinated-molecules reliable BDE values are reported with estimated 95% confidence limits ranging from 3.7 to 7.5 kJ.mol⁻¹.

Correlation equations of experimental/literature vs. calculated BDE values were also obtained (13-15) where the best correlations were observed for the CCSD(T)/SPK-ATZP method and for the evaluated BDE's (Table 4):

$$\text{BDE}(\text{C-X})_{(\text{experimental})} = 1.0179 \cdot \text{BDE}(\text{C-X})_{\text{MP2/SPK-ATZP_Table 4}} - 7.1392; R^2 = 0.9956 \quad (13)$$

$$\text{BDE}(\text{C-X})_{(\text{experimental})} = 0.9954 \cdot \text{BDE}(\text{C-X})_{\text{CCSD(T)/SPK-ATZP_Table 4}} + 6.8619; R^2 = 0.9965 \quad (14)$$

$$\text{BDE}(\text{C-X})_{(\text{experimental})} = 1.0083 \cdot \text{BDE}(\text{C-X})_{\text{evaluations_Table 4}} - 2.0992; R^2 = 0.9965 \quad (15)$$

These correlation equations include the iodinated molecules of Table 4 with known experimental BDE values. The BDE values of the molecules of Table 4 - illustrated in Figure 5 - show excellent correlation with the experimental values. The corresponding linear equations (13), (14) and (15) have R^2 values 0.9956, 0.9965 and 0.9965 respectively.

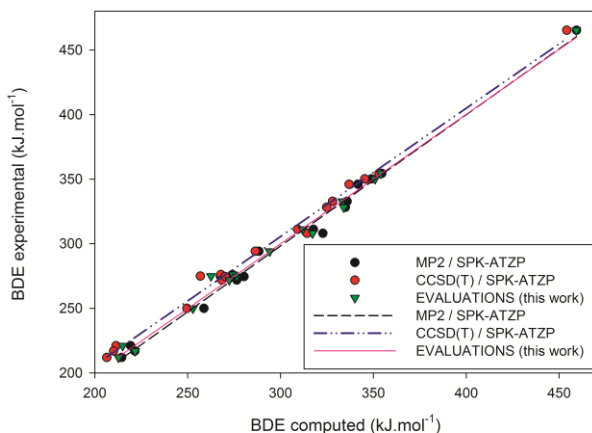


Figure 5. Carbon-halogen BDE (C-X, X=F, Cl Br, I) of the molecules in Table 4 obtained at MP2/SPK-ATZP & CCSD(T)/SPK-ATZP levels of theory and by evaluations (this paper) vs. their corresponding experimental values (kJ.mol⁻¹).

On the basis of these results, the method described above, together with isodesmic reactions to remove errors, may profitably be used to obtain very accurate standard molar enthalpies of formation of halomethane species.

CONCLUSIONS

In this study standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ and carbon-halogen BDE of a set of halogen-containing organic species with atmospheric importance have been calculated. Ab initio calculations were performed at the DFT, MP2 and CCSD(T) levels of theory via isodesmic reaction schemes which can provide very high systematic error compensation. The obtained results were compared to theoretical as well as experimental data available in the literature and thermochemical databases. In all cases, excellent correlations were observed and reliable $(\Delta H_f^\circ)_{m(g)}$ average values of the species studied were obtained by extrapolating their theoretical values from the corresponding correlation equations and isodesmic reactions.

The application of isodesmic reactions to remove the systematic errors yields $(\Delta H_f^\circ)_{m(g)}$ that are in close agreement with experimental values, with rms deviations that range from 2.8 kJ.mol⁻¹ [CCSD(T)] to 5.1 kJ.mol⁻¹ [MP2] which is well below the rms experimental uncertainty of 16.1 kJ.mol⁻¹. Similarly, the calculated $(\Delta H_f^\circ)_{m(g)}$ values for the corresponding halomethane radicals are found to be in close agreement with experimental values, with rms deviations that range from 4.1 kJ.mol⁻¹ [MP2] to 5.7 kJ.mol⁻¹ [CCSD(T)] which is close the rms experimental uncertainty of 5.2 kJ.mol⁻¹.

The reliable average carbon-halogen BDE values are also in close agreement with experimental values with rms deviation 4.9 kJ.mol⁻¹ which is well below the rms experimental uncertainty of 8.2 kJ.mol⁻¹.

Based on this approach, new estimates for standard molar enthalpies of formation and BDE are suggested including for species that to our knowledge there are no experimental $(\Delta H_f^\circ)_{m(g)}$ (CHCl₂Br, CHBr₂Cl, CHBrCl, CHICl, CHIBr) or BDE values (CHCl₂Br, CHBr₂Cl, CHBrCl, CHICl, CHIBr) available in the literature. Reliable $(\Delta H_f^\circ)_{m(g)}$ and BDE average values are also suggested for several halomethanes where literature experimental or evaluation data have large error bars (>10 kJ).

On the basis of these results, it is concluded that these calculational procedures at the MP2 and particularly at the CCSD(T) level, together with isodesmic reactions and correlation and regression analysis may be used to obtain accurate standard molar enthalpies of formation $(\Delta H_f^\circ)_{m(g)}$ and carbon-halogen BDE of halomethane species.


DISCLOSURE STATEMENT

No potential conflict of interest is reported by the author.

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