Thermochemistry of halogen-containing organic compounds with influence on atmospheric chemistry

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ABSTRACT

We report a study on the thermochemical properties of a wide variety of halogen-containing organic compounds with relevance on several atmospheric chemical processes, such as catalytic ozone destruction. In particular, we have computationally determined the standard molar enthalpies of formation, \( \Delta_f H_m(g) \), and the carbon-halogen bond dissociation enthalpies, \( BDE \), in the gas phase at 298.15 K. A reliable estimation of these thermodynamic magnitudes was deduced, using atomization and isodesmic reactions methodologies, from \textit{ab initio} computational methods. The enthalpies of formation of the radicals formed through bond dissociations have also been computed.

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1. Introduction

Halogenated organic species are emitted into the atmosphere from a variety of sources of both natural and anthropogenic origin. The lifetime of these species ranges from less than 6 months for Very-Short Lived species (VSLs), to several years for Long-lived (LL) species [1]. The natural source of halogenated hydrocarbons, e.g. bromoform (CHBr3), has been found to be marine phytoplankton [2] and seaweed [3], while anthropogenic sources arise from chemical products widely used in many industrial and domestic applications [4].

The breakdown products (i.e. halogen atoms and oxides) of VSL and LL species can alter the oxidative capacity of the atmosphere through several processes [5,6]: (i) ozone destruction involving catalytic cycles; (ii) changes in the partitioning of HOx and NOx; (iii) the oxidation of dimethyl sulphide (DMS) and iv) the oxidation of elemental mercury (Hg0 → HgII). Of special significance is the stratospheric ozone destruction caused by both anthropogenic emissions of LL sources such as halons [7], and oceanic emissions of VSLs [8].

Modeling of the atmospheric chemistry of halogenated hydrocarbons requires also reliable thermochemical data, such as enthalpies of formation, \( \Delta_f H_m(g) \) and bond dissociation enthalpies, \( BDE \). Calorimetry, kinetic, photoelectron spectroscopy and photoionization mass spectrometry, e.g. photoion-photoelectron coincidence

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iii) To determine the intrinsic accuracy of our methodology for predicting thermochemical properties of halogenated organic compounds of atmospheric interest.

iv) To expand the existing database of thermochemical properties of halogenated organic species, so that the inclusion of the obtained parameters in atmospheric models helps to further improve our understanding of the atmospheric impacts of these species.

The set of the studied halogenated organic species includes CHBr3, CH2Br2, CH3Br, CH2BrCl, CHCl3Br, CHBr2Cl, CH2Cl2, CH2BrCl, Cl2C=CCl2, ClICH=CCl2, CHCl3HCl2, Cl2C-O, ClHC=O, CH3l, CH2I2, CH2ICl, CH2IBr. These species, and their breakdown products, contribute to ozone destruction in both troposphere and stratosphere [1], and may be a link between climate change and tropospheric ozone [25].

2. Computational methods

Standard ab initio molecular orbital calculations [26] were performed with the Gaussian 09 series of programs [27]. The energies of the compounds studied were computed using two different theoretical model chemistry Gaussian- 

of the compounds studied were computed using two different the-

formed with the Gaussian 09 series of programs [27]. The energies at 298.15 K for the compounds studied in this work are collected and zero-point energy corrections. Energies at 0 K and enthalpies corrects many of the deficiencies of the G

G4 [29] levels. Note that G3 theoretical procedure modifies and tropospheric ozone [25].

stratosphere [1], and may be a link between climate change and

methanes (CH2Br2, CH2BrCl, CH2I2, CH2IBr and CH2ICl) with a pre-

iodine-loss processes of C2H4I2

We also present those collected in reviews and evaluations. The particular of CH2BrxI2-x dihalomethanes, has been checked and reliable experimental

D

obtained from combustion, vaporization and reaction calorimetric

D

known experimental

D

D

3. Results and discussion

3.1. Enthalpies of formation \( \Delta f m(g) \) of neutrals

3.1.1. Experimental values

Table 1 lists the available experimental values of \( \Delta f m(g) \) for the set of halogen-containing compounds studied in this work. We also present those collected in reviews and evaluations. The most reliable values of \( \Delta f m(g) \) are written in bold.

In the case of dihalomethanes, there is a good agreement among known experimental \( \Delta f m(g) \) values of CH2Cl2, which were obtained from combustion, vaporization and reaction calorimetric measurements [12,13]. Lago et al. [32] taking the recommended \( \Delta f m(g) \) of this compound and TPEPICO (Thermochetical-Photoelectron-Photoion Coincidence Spectroscopy) results, derived reliable experimental \( \Delta f m(g) \) values for five neutral dihalomethanes (CH2Br2, CH2BrCl, CH2I2, CH2IBr and CH2ICl) with a precision better than 3 kJ mol^{-1}. The self consistency of them, in particular of CH2Br2I2, dihalomethanes, has been checked and confirmed by other results [33], although Baer et al. [34] proposed to revise the \( \Delta f m(g) \) of CH2I2, changing to 113.5 \pm 2.0 kJ mol^{-1}, on the basis of both experimental (TPEPICO) and theoretical ab initio groups in order to obtain a good consistency of their results on iodine-loss processes of C2H4I2 cations.

For CH3Br, we have recommended the \( \Delta f m(g) \) consigned by Kuchcadler-Kuchcadler [35] which considers the values reported by Pedley [13], Cox-Pilcher [36] and in NIST [12]. For CH3Cl, CHCl3, Cl2C=CCl2, ClICH=CCl2 and ClICH2CH2Cl, according to Manion [37] criteria, we recommend values of NIST [12]. For CH4I, we consider reliable and updated the \( \Delta f m(g) \) deduced by Bodi et al. [38] from iPEPICO (Imaging-Photoelectron-Photoion Coincidence Spectroscopy) results.

To our knowledge, for two of the species, CHCl3Br and CHBrCl there are no experimental \( \Delta f m(g) \) available in the literature. In the case of CHCl=O, Gurvich et al. [17] reported an estimated \( \Delta f m(g) \) with high uncertainty (\pm 20 kJ mol^{-1}), which is excluded as a reliable experimental datum. Therefore, the \( \Delta f m(g) \) of the three compounds described above have been computed.

3.1.2. Computed values

\( \Delta f m(g) \) of only chloro- and/or bromo-containing compounds have been evaluated using the G3 and G4 model chemistries. The standard procedure to obtain \( \Delta f m(g) \) in Gaussian-n theories is through atomization reactions [39].

Several authors [40–42] have shown that more accurate \( \Delta f m(g) \) can be derived using isodesmic or homodesmotic [43] reactions rather than atomization energies. The cancellation of errors for such cases involving similar chemical bonds improves the agreement with the experiment. Ragavachari et al. [44] proposed to use a standard set of isodesmic reactions, the “bond separation (BS) reactions”, to derive the theoretical \( \Delta f m(g) \). BS reactions are those where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same types of linkages. Thus, for example, the BS reaction for CHCl3Br is:

\[
\text{CHCl3Br} + 2 \cdot \text{H} \rightarrow 2 \cdot \text{CHCl} + \text{CH3Br}
\]

(1)

For three compounds, additional isodesmic reactions have been used, reactions (2)–(4) for CHCl3Br, CHBr2Cl and ClHC=O, respectively:

\[
\begin{align*}
\text{CHCl3Br} + \text{H} & \rightarrow \text{CHCl3} + \text{CH3Br} \\
\text{CHBr2Cl} + \text{H} & \rightarrow \text{CHBr2} + \text{CHCl} \\
2 \cdot \text{ClHC} & \rightarrow \text{H}2\text{C} + \text{O} + \text{Cl2C} = \text{O}
\end{align*}
\]

(2–4)

\( \Delta f m(g) \) of the studied compounds, computed using atomization and isodesmic reactions (at G0 level) are collected in Table 1. As shown, except for CHBr3, there is a very good agreement between recommended experimental and computed values, particularly using G4 methodology where the deviations between theoretical and experimental data are less than 3 kJ mol^{-1}. These values are also consistent with those reported in the literature and obtained from e.g. CCSD calculations (see Table 1). For CHBr3 the deviations among experimental and computed G0 values can be up to 14 kJ mol^{-1}. It is noteworthy that the \( \Delta f m(g) \) of this compound estimated by Burcat et al. [45], using the DK-CCSD(T) method, is the closest to the experimental recommended value.

As shown in Fig. 1, \( \Delta f m(g) \) computed from G0 methodologies using both atomization (atom) and bond separation (BS) reactions schemes correlate very well with the corresponding experimental values, as shown by Eqs. (5)–(8), being the best correlations those using G4 methods.

\[
\begin{align*}
\Delta f m(g)_{\text{exp}} & = 1.0248 \cdot \Delta f m(g)_{\text{G3, atom}} + 3.78; \ n = 11, \\
R & = 0.9985, \ \text{sd} = 4.35 \text{ kJ \cdot mol}^{-1} \ \text{(5)} \\
\Delta f m(g)_{\text{exp}} & = 1.0074 \cdot \Delta f m(g)_{\text{G3, BS}} + 4.08; \ n = 9, \\
R & = 0.9992, \ \text{sd} = 3.47 \text{ kJ \cdot mol}^{-1} \ \text{(6)} \\
\Delta f m(g)_{\text{exp}} & = 1.0059 \cdot \Delta f m(g)_{\text{G4, atom}} + 0.16; \ n = 11, \\
R & = 0.9994, \ \text{sd} = 2.70 \text{ kJ \cdot mol}^{-1} \ \text{(7)} \\
\Delta f m(g)_{\text{exp}} & = 1.0159 \cdot \Delta f m(g)_{\text{G4, BS}} + 1.87; \ n = 9, \\
R & = 0.9995, \ \text{sd} = 2.70 \text{ kJ \cdot mol}^{-1} \ \text{(8)}
\end{align*}
\]
Since G3 and G4 methods are not available for iodine, the energy of iodine-containing compounds has been computed using alternative MP2 and QCISD methods. Optimization and frequency calculations have been carried out at the MP2/QZVP level of theory, which is available for iodine, and also QCISD(T)/QZVP single point calculations on the MP2/QZVP optimized geometries. As shown in Table 1, the theoretical $\Delta_{f}H_{m}^{\circ}$ of these compounds, calculated using BS scheme, are very close to the experimental values, the largest difference between both values being 5.3 kJ mol$^{-1}$ in the case of CH$_2$I$_2$, at the MP2 level. However, the atomization reaction scheme gave poorer results at these levels, and they are not included in Table 1.

The MP2 and QCISD methods were also extended to evaluate, using BS schemes, the $\Delta_{f}H_{m}^{\circ}$ of chloro- and bromo-containing...
practically the same that one obtained by Nagy et al. [46] from Fig. 2. Differences between experimental and theoretical values are high, the results obtained with G(Eqs. (9) and (10)) are obtained:

\[ \Delta H_f^0(\text{exp}) = 1.0043 \cdot \Delta H_f^0(\text{MP2}) + 4.89; \quad n = 12. \]
\[ R = 0.9989, \text{sd} = 4.57 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ \Delta H_f^0(\text{exp}) = 1.0001 \cdot \Delta H_f^0(\text{QCISD}) - 4.63; \quad n = 12. \]
\[ R = 0.9989, \text{sd} = 4.52 \text{ kJ} \cdot \text{mol}^{-1} \]

Note that the use of MP2 and QCISD methods does not improve the results obtained with Gn levels of theory. In some cases, the differences between experimental and theoretical values are high, almost 14 kJ mol\(^{-1}\) for ClC = CCl\(_2\), and 12 kJ mol\(^{-1}\) for CICH = CCl\(_2\) and CHBr\(_3\).

Table 1 also reports the reliable \(\Delta H_f^0(g)\) average values (in kJ mol\(^{-1}\) for CHCl\(_2\)Br = \(-50.9 \pm 2.4\), CHBr\(_2\)Cl = \(-1.0 \pm 3.1\) and CICH = O = \(-184.3 \pm 1.8\)), which are obtained in this work, by extrapolating their theoretical values, from correlation Eqs. (5)–(10) and isodesmic reactions 2–4. The associated uncertainties correspond to the standard deviations of the mean for ten computed values. The \(\Delta H_f^0(g)\) of CICH = O determined and recommended by us is practically the same that one obtained by Nagy et al. [46] from CCSD(T) high level calculations. This result supports the reliability of our calculations.

3.2. Enthalpies of formation of radicals. Carbon-halogen bond dissociation enthalpies, BDEs

The BDEs of a molecule are the most important thermodynamic properties that rule reactivity. The homolytic X–Y bond cleavage enthalpy of reaction at 298.15 K [54] is defined as BDE(X–Y),

\[ X-Y \rightarrow X + Y \quad \Delta H_f^0(\text{g}(11)) = \text{BDE}(X-Y) \]

where X and Y are the organic free radicals of the molecule XY.

The experimental measurement of BDEs is not easy and requires a great deal of care. Usually experimental BDEs values are derived from \(\Delta H_f^0(g)\) of XY neutral molecule and their corresponding X- and Y- radicals, which in turn are derived from parameters determined with kinetic (e.g. of competitive halogenation reactions), photodissociation or acidity/electron affinity techniques and completed with auxiliary thermochemical data. The accuracy of all these values is key to determine a reliable experimental \(\Delta H_f^0(g)\) of the radical considered. It is important to mention that the determination of physical and chemical parameters of radicals and radical reactions is still challenging. In general, experimental and theoretical inaccuracy for open-shell species, such as radicals, is usually larger than that for closed-shell species.

\(\Delta H_f^0(g)\) of organic radicals reported in this work were taken from the most recent review of thermodynamic data available (see Table 2) and several of them have been revised and updated. Note that for CHBr, the experimental \(\Delta H_f^0(g)\) available values are very similar, and therefore we take an average value (169.4 ± 3.0 kJ mol\(^{-1}\)) as a recommended \(\Delta H_f^0(g)\). The associated uncertainty is twice the standard deviation of the mean.

As for CH₂Cl, using the data from the dissociative photoionization of CH₂CIBr [55], we have derived a value of \(\Delta H_f^0(g) = 115.8 \pm 2.2 \text{ kJ} \cdot \text{mol}^{-1}\). This value is in good agreement with those determined by Holmes and Loosing [64] (appearance energy measurements) and Seetula [57] (kinetic measurements), but 6 kJ mol\(^{-1}\) lower than the uncorrected value reported by Tschuiakov-Roux and Paddison [58] (kinetic measurements).

For CH₂C₁, Tschuiakov-Roux and Paddison [58] also determined an overestimated \(\Delta H_f^0(g)\); we correct and reevaluate this value, which is close to the one determined by Seetula [57]. Both values agree well with recommended \(\Delta H_f^0(g) = 87.1 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}\) obtained by Lago and Baer [59] from TPEPICO results.

In the case of CHBr₂, Seetula and Eskola [60] determined an experimental \(\Delta H_f^0(g) = 199.1 \pm 2.7 \text{ kJ} \cdot \text{mol}^{-1}\), but considering in their thermochemical derivations a theoretical \(\Delta H_f^0(g)\) value for CHBr₂. By using more recent data, we propose for this radical a new reevaluated \(\Delta H_f^0(g) = 197.8 \pm 4.3 \text{ kJ} \cdot \text{mol}^{-1}\). This outcome agrees well with that estimated by Tschuiakov-Roux and Paddison [58], once their value is corrected and reevaluated according to Seetula and Eskola [60] notes.

Dobé et al. [61], from kinetic measurements, derived the \(\Delta H_f^0(g)\) of CHBrCl (140 ± 4 kJ mol\(^{-1}\)) taking into account a theoretically estimated \(\Delta H_f^0(g)\) of CH₂CIBr. Replacing the latter value by the recommended experimental datum, leads to an updated value of 144.4 ± 3.7 kJ mol\(^{-1}\) for CHBrCl, which in turn is close to that reported by Seetula [50].

Nicolivich et al. [62] derived the \(\Delta H_f^0(g)\) of COCI, from measurements of kinetic of its formation/decomposition, as \(-21.8 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}\). On the other hand, Terentis and Kable [63] determined, from photolysis of H₂CO, the \(\Delta H_f^0(g)\) of formyl radical ‘HCO, equal to 42.5 ± 0.5 kJ mol\(^{-1}\), which is close to those reported in NIST. The \(\Delta H_f^0(g)\) of both COCI and HCO radicals are more accurate and, respectively almost 5 and 9 kJ mol\(^{-1}\) higher than those evaluated by Holmes and Loosing [64]. These latter values have high uncertainty (± 8.4 kJ mol\(^{-1}\)) and were derived from
appearance energy measurements and estimated $\Delta H_m^\circ(g)$ of both, counter ions (CH$_2$OH$^-$) and precursor molecules (R-CH$_2$OH).

For CH$_3$J, there is a good agreement between the two experimental $\Delta H_m^\circ(g)$ values, close to 229 kJ mol$^{-1}$, derived by Holmes and Loosing [56,64] and Seetula [65] (kinetic measurements involving CH$_3$J). Furuyma et al. [66] also derived, from iodination kinetic experiments, a value of 230.1 ± 6.7 kJ mol$^{-1}$, but taking into account an overestimated value of $\Delta H_m^\circ(g)$ for CH$_2$I$_2$. The new updated value for CH$_3$J is $\Delta H_m^\circ(g) = 215.7 ± 6.7$ kJ mol$^{-1}$. Updating also the value obtained by De Corpo et al. [67] from electron impact experiments of CH$_2$I$_2$, we obtain a result of 213.7 kJ mol$^{-1}$.

We recommend the reevaluated value of Furuyma et al. [66] which agrees with those obtained by Marshall et al. [47] and Louis et al. [68,69] using QCISD and DK-CCSD(T) levels of theory, respectively.

As illustrated in Fig. 3, the $\Delta H_m^\circ(g)$ of organic radicals computed from G4 methodologies using atomization (atom) schemes correlate very well with the experimental values, as shown by Eqs. (12) and (13), being the best correlation the obtained using G4 method.

$\Delta H_m^\circ(g)_{\text{exp}} = 1.00290 \cdot \Delta H_m^\circ(g)_{\text{G3, atom}} + 0.43; \ n = 10, R = 0.9980, \text{sd} = 5.3 \text{ kJ} \cdot \text{mol}^{-1}$ (12)

$\Delta H_m^\circ(g)_{\text{exp}} = 1.00398 \cdot \Delta H_m^\circ(g)_{\text{G4, atom}} + 1.81; \ n = 10, R = 0.9991, \text{sd} = 3.9 \text{ kJ} \cdot \text{mol}^{-1}$ (13)
Table 3
BDE(C–X; X = Cl, Br, I) values, experimental and calculated at G4 (n = 3,4) and QCISD(T)/QZVP//MP2/QZVP levels of theory. The most reliable values are written in bold.

<table>
<thead>
<tr>
<th>Species</th>
<th>BDE (C–Cl)/kJ mol⁻¹</th>
<th>G3</th>
<th>G4</th>
<th>QCISD</th>
<th>Exp.</th>
<th>Evaluations</th>
<th>G3</th>
<th>G4</th>
<th>QCISD</th>
<th>Exp.</th>
<th>Evaluations</th>
</tr>
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<tbody>
<tr>
<td>CHBr3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>258.8</td>
<td>253.1</td>
<td>265.2</td>
<td></td>
<td>274.9 ± 13.0, 271.1, 254.3 ± 5.4, 280.3, 278.1 ± 4.5, 291.6, 296.3 ± 1.1</td>
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<tr>
<td>CH2Br2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>277.3</td>
<td>270.5</td>
<td>286.9</td>
<td></td>
<td>276.1 ± 5.3, 275.3 ± 3.3, 292.0 ± 8.4</td>
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<td></td>
<td>315.4</td>
<td>311.0</td>
<td>309.3</td>
<td></td>
<td>308 ± 17, 320 ± 5.3</td>
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<tr>
<td>CH2BrCl</td>
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<td></td>
<td></td>
<td></td>
<td>315.7</td>
<td>311.9</td>
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<td>328.4</td>
<td>323.2</td>
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<td>383.7, 478.2 ± 5.2</td>
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<td>398.0</td>
<td>394.3</td>
<td>402.1</td>
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<td>391.6, 400.3 ± 4.2</td>
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<td>314.7</td>
<td>308.3</td>
<td>308.8</td>
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<td>311.1 ± 2.0, 307.9, 316.3, 311.3 ± 2.6</td>
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<td>350.0</td>
<td>348.0</td>
<td>349.1</td>
<td></td>
<td>341.5 ± 5.0, 331.0, 346.3 ± 4.2</td>
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<td>Cl2C = CCl2</td>
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<td>323.0</td>
<td>320.4</td>
<td>317.8</td>
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<td>318.8 ± 8.4, 319.6 ± 2.7</td>
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<td></td>
<td></td>
<td>347.2</td>
<td>344.8</td>
<td>344.5</td>
<td></td>
<td>348.1 ± 1.9</td>
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<td>CHCl2</td>
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<td></td>
<td></td>
<td>328.0</td>
<td>328.2 ± 6.9</td>
<td>326.3 ± 6.7</td>
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</tbody>
</table>

The ΔHm(g) of CH3Cl, CH2Cl2 and CHCl = O computed here are in good agreement with those obtained at CCSD(T) high level of theory [49,52,69]. Somewhat surprisingly, CCSD(T) calculations of Lazarou et al. [48] have large deviations respect to experimental values, particularly for ΔHm(g) of CHCl2. According with Feller et al. [49] it would be due to the relatively small size of their used basis sets calculations.

The radical ‘CCl = CCl2 formed in the homolytic bond cleavage of C2Cl4 has been excluded in all our correlations because there is a difference of ca. 140 kJ mol⁻¹ between experimental and theoretical ΔHm(g) values. Its experimental ΔHm(g) = 190 ± 50 kJ mol⁻¹, estimated by Gurvich et al. [17], has a large uncertainty, so it would not be considered as a reliable datum. In the case of ‘CH = CCl2, its ΔHm(g) is not reported in the literature. Accordingly, for both ‘CCl = CCl2 and ‘CH = CCl2 radicals, we recommend ΔHm(g) = 200 ± 1 kJ mol⁻¹, respectively in kJ mol⁻¹, 332.6 ± 2.6, 271.1b, 266.9, 254.3 ± 5.4, 280.3, 278.1 ± 4.5, 291.6, 296.3 ± 1.1, 258.6 ± 4.8, 280.3, 278.1 ± 4.5, 291.6, 296.3 ± 1.1, 258.6 ± 4.8.

The largest deviations among experimental and theoretical values are given for CH2Br2: up to 9.9 and 7.4 kJ mol⁻¹ respectively for G3 and G4 methodologies. It is important to note that ΔHm(g) of this radical evaluated by Burcat et al. [45] and Lazarou et al. [48], at CCSD(T) level of theory, are very close to the experimental recommended value (deviations less than 3.8 kJ mol⁻¹), while that computed by Marshall et al. [47], at QCISD level, gives a deviation comparable to the obtained by us at G4 method.
molecules and their corresponding radicals (Eq. (11)). The direct BDE experimental measurements are scarce. We can mention the following works: i) Chen et al. [76] determined, using electron capture technique and electron affinity data, the BDEs of halogen organic compounds such as CH₂Cl, CH₃Cl, CHCl₃, CH₂Br₂ and CHI in good agreement with the updated BDEs reported here (deviations less than 7 kJ mol⁻¹). ii) Li et al. [55] derived, from PFI-PEPICO and adiabatic ionization energy measurements, the bond dissociation energy of CH₂BrCl, at T = 0 K, as D₀ (C-Br) = 266.3 ± 1.0 kJ mol⁻¹. The conversion to 298.15 K, made in this work using average data of thermal enthalpies (H₂98m⁰ - H₂m⁰) determined by Gn calculations, lead to a recommended experimental BDE (C-Br) = 271.8 ± 1.0 kJ mol⁻¹. This value is 5.5 kJ mol⁻¹ lower than the reported by Lago et al. [32], which was derived considering an over-estimated ΔH₂m⁰(g) of CH₂Cl computed by Lazarou et al. [48].

BDE(C-Cl) and BDE(C-Br) directly evaluated at the G3 and G4 methods, are listed in Table 3. For both methods, there are good agreement between theoretical and available experimental BDE (C-X, X = Cl, Br) values, the largest difference between both is less than 8.5 kJ mol⁻¹. Correlation equations, depicted in Fig. 4, are now obtained and one can see that the best correlation is given for G4 method:

\[
\begin{align*}
BDE(C-\text{X}, \text{exp}) & = 1.01594 \cdot BDE(C-\text{X}, G3) - 5.60; \quad n = 17, \\
R & = 0.9981; \quad sd = 3.62 \text{ kJ mol}^{-1} \\
BDE(C-\text{X}, \text{exp}) & = 0.99526 \cdot BDE(C-\text{X}, G4) + 4.95; \quad n = 17, \\
R & = 0.9987; \quad sd = 3.04 \text{ kJ mol}^{-1} \\
BDE(C-\text{X}) & \text{ including also iodinated-compounds have been computed at the QCISD(T)/QZVP/MP2/QZVP level of theory (see Table 3). For chlorinated and brominated species, these values agree acceptably with the corresponding experimental ones; while for iodinated molecules, there is a good agreement only for BDE (C-Cl) of CH₂ICl. The correlation equation between experimental and QCISD calculations of BDE(C-\text{X}) is given by:}
\end{align*}
\]

\[
\begin{align*}
BDE(C-\text{X}, \text{exp}) & = 1.08898 \cdot BDE(C-\text{X}, \text{QCISD}) - 29.64; \\
R & = 0.9828; \quad sd = 6.85 \text{ kJ mol}^{-1} \\
\end{align*}
\]

4. Conclusions

Experimental and theoretical ΔH₂m⁰(g) and carbon-halogen BDE of a set of halogen-containing organic species with atmospheric relevance have been revised and updated. In this study, theoretical calculations have been performed, by means of atomization and isodesmic reaction methods, using Gn (n = 3, 4), MP2 and QCISD levels of theory. The obtained results are discussed and compared to theoretical as well as experimental data available in databases and in literature.

Gn (n = 3, 4) methodologies, particularly G4 have been shown to be an accurate theoretical method to provide reliable ΔH₂m⁰(g) and BDE(C-\text{X}) values for chlorinated and brominated species. In several cases these values are very close to those obtained by the most accurate, and consequently most time consuming, methods such as coupled-cluster CCSD(T) level of theory. Only for a few iodinated-molecules the QCISD method has been proven reliable for thermochemical values. We suggest that for these molecules, new theoretical revisions are necessary, with high-accuracy calculations.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2016.11.009.

References


This correlation includes, for iodinated molecules, only the BDE (C-\text{Cl}) values of CH₂ICl. The use of QCISD theory do not improve the results obtained with Gn methodologies. For this level of calculations, the largest difference between theoretical and experimental BDE (C-X) values can be up to 11.2 kJ mol⁻¹. We should also note that the standard deviation of the correlation line increases from 3.04 to 6.85 kJ mol⁻¹ from the G4 to QCISD calculations. It is interesting to mention that North et al. [77] determined, at MP2-CCSD(T) levels of theory, BDE(C-\text{X}) values for CH₂Br₂, CH₂Br, CH₂Cl₂ and CHCl₃, which are close to the experimental ones (deviations less than 5 kJ mol⁻¹). Nevertheless, for CHBr₃ and CH₃Cl their computed BDE(C-\text{X})s are far from experimental data, e.g. 12.6 kJ mol⁻¹ for CHBr₃. For this case, the difference is even higher if we compare with the BDE(C-\text{Br}) value recently determined by Rosokha et al. [78] at G3(MP2)-RAD(+) level of theory.
